National Park Service
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Northeast Region
Boston, Massachusetts

Understanding Atmospheric Deposition to Complex Landscapes at Acadia National Park, Maine 2002-2005

Technical Report NPS/NER/NRTR—2007/080

ON THE COVER
A hemispherical canopy photo of site C4C, a mixed-vegetation site, in Cadillac Brook watershed, summer 2004.
Photograph by: Sarah J. Nelson, University of Maine

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G. K. Sheehan litterfall mercury technical report

Abstract

This project provided a continuation of the 1999-2005 record of major ion and Hg chemistry in throughfall and streamwater, and the hydrologic fluxes, for a pair of intensively studied watersheds at Acadia National Park. Research on selected landscape factors influencing the amount of chemical deposition in these watersheds indicated that canopy openness, vegetative cover composition, and elevation were the most important landscape variables for predictive modeling of major ion and Hg deposition. A notable exception was NO_3, where landscape variables did little to help prediction of wet deposition. We used a regression tree model approach to predict atmospheric deposition of SO_4 and Hg using these landscape factors. We surveyed streams across the Park, some of which had not been sampled since the 1980s, and coordinated key stream water quality data sets into a single database. Comparison of modeled deposition across the Park and streamwater survey data suggested that although the deposition of Hg and SO_4 appeared to be controlled by the same landscape factors (vegetation structure and elevation), spatial patterns in streamwater chemistry for these two analytes were not the same. Streamwater SO_4 appeared to generally follow deposition patterns. Streamwater Hg was highest in association with lowland and wetland landscape features. Another focus of this research was temporal patterns in atmospheric deposition, particularly for Hg. Research in other areas of the US had suggested that Hg deposition was minimal in winter, yet winter deposition of Hg using wet-only collectors was approximately one-quarter of annual wet deposition flux at Acadia. This places a greater emphasis on winter deposition monitoring in order to evaluate ecosystem exposure for Hg, although further research is necessary to understand Hg deposition in winter, such as losses via volatilization.

EXECUTIVE SUMMARY

Introduction

One of the purposes of the Clean Air Act is to preserve, protect, and enhance the air quality in national parks and wilderness areas, and as a result the Act designates national parks as Class I areas subject to the most stringent air quality requirements. Under the Organic Act, the National Park Service is responsible for protecting air quality and natural resources that might be affected by air pollution.

Air quality is a major management issue at Acadia National Park, which is located on Mount Desert Island on the coast of eastern Maine. Acadia's steep slopes, high peaks, and proximity to coastal storms and fog create an environment conducive to the interception of polluted air masses. Weather patterns move eastward across the United States, passing over industrialized areas in the Ohio and St. Lawrence River valleys before converging over northeastern North America and moving out to sea. Acadia National Park is located in this pathway, and atmospheric contaminants transported over long distances are of particular concern for park managers.

For example, elevated deposition of Hg and acid rain-forming chemicals has been well-documented at Acadia. High levels of Hg in Acadia's fish and wildlife indicate that deposition of atmospheric contaminants is affecting biota and ecosystems of the region. To understand watershed processes affecting contaminant deposition and cycling, we established a pair of gauged watershed research sites at Acadia in 1998 as part of the Park Research and Intensive Monitoring of Ecosystems Network (PRIMENet), a joint program of the U.S. EPA and the National Park Service. The Acadia watersheds offer a regionally diverse variety of characteristics, ranging from mature softwood forests to regenerating hardwoods after a fire, all on homogeneous bedrock with similar slopes and aspects. Hadlock Brook watershed, the "control" site, has remained undisturbed by fire or land clearing for 500 years or more, and is dominated by mature coniferous forest. Most of Cadillac Brook watershed burned in an intense wildfire in 1947, and land cover in the watershed is dominated by successional mixed forest.

Objectives

Research in the paired watersheds from 1999-2001 showed that landscape attributes influence deposition of Hg, sulfate (SO_4), nitrate (NO_3), and other major ions. Building on this work, we continued research at the two watersheds from 2002-2005 to address several different, but related questions:

1. How does the landscape influence the deposition of atmospheric contaminants?
2. How much Hg enters the watershed via falling leaves, needles, and twigs?
3. How does proximity to the ocean influence seasonal patterns of deposition?
4. Does stream water chemistry reflect patterns of deposition?

1. How does the landscape influence the deposition of atmospheric contaminants?

Chemical deposition to the landscape is typically evaluated based on measuring chemicals in precipitation. Yet for Hg and other conservative ions, dry deposition—the amount of a chemical that settles to the landscape attached to dust and other particles or is absorbed—can equal or exceed wet deposition. Throughfall is a collective term for the precipitation and dry matter that falls through the forest canopy; throughfall measurement represents the sum of wet and dry deposition. This approach allows for a more complete investigation of watershed processes, as it includes the interaction of the landscape (e.g., land cover, slope, aspect, elevation) with the atmosphere. A throughfall approach recognizes the heterogeneity inherent in forested, mountainous areas with diverse, often patchy land use histories, as is the case with Acadia National Park.

In the first three years (1999-2001) of the watershed research program, we sampled 80 individual throughfall sites. Earlier research at these throughfall sites indicated that vegetation type, elevation, and aspect were important drivers for chemical deposition distribution, but traditional statistical methods did not adequately represent some landscape features, such as the heterogeneity of coniferous communities at different elevations. Incorporating landscape information into a model that could predict deposition remained a challenge. To scale up from the watershed level to the entire park, we needed to continue monitoring the watersheds while also examining landscape factors more closely. Using cluster analysis to select a representative site from each major landscape-chemical condition, we created a revised set of 21 throughfall sites for continued monitoring.

The results showed that for Hg, the range in rain throughfall concentration for 2004 was 2.06-36.6 ng/L, with a mean of 12.8 ng/L. Only 5% of the 555 observations in 1999-2000 were greater than the maximum of 36.6 ng/L reported for the 2004 data set, and we concluded that the smaller set of sites adequately represented the range of chemical concentration, and would be adequate for long-term monitoring of throughfall, or periodic re-validation of model results.

We continued monitoring throughfall and streamwater chemistry in the paired watersheds. Using new canopy cover data, we re-evaluated controls on throughfall deposition. Canopy openness (or vegetation type) and elevation were the most important landscape variables describing variability in deposition of major ions and Hg (this is not the case for NO_3, which is not described well by landscape features).

Based on the landscape relationships with throughfall deposition, we modeled deposition of SO_4 and Hg across the entire park, using relationships from the small watersheds and a multivariate regression tree model that depended heavily on canopy openness and elevation. The importance of canopy openness has not been discussed in the literature, and merits further investigation. Regression tree analyses supported including vegetation structure in deposition models, and indicated that canopy height may be used as a surrogate for canopy coverage if further site specific validation is conducted. **The model provides further evidence that vegetation characteristics and elevation are the most important landscape factors affecting throughfall variability at Acadia.**

This project laid the groundwork for creating more accurate, spatially explicit deposition estimates for several ions across Acadia National Park. We found significant correlations

between major ions that suggest **modeling approaches developed for S can be applied to some other ions and Hg.** We calculated new landscape metrics, and determined which landscape factors control variability in deposition across the two small watersheds. **While vegetation type was still an important determinant for deposition of most major ions and Hg, the newly-measured canopy openness variable was equally or more important for Hg and SO_4.** Although canopy openness requires measurement at each individual site, early results suggest that canopy height, available for the entire park as an attribute of the USGS-NPS vegetation mapping project GIS coverage, could be a reasonable surrogate for canopy openness.

2. How much Hg enters the watershed via falling leaves, needles, and twigs?
Hg deposition to the landscape is typically evaluated using precipitation data. Yet fallen leaves, needles, and twigs ("litterfall") are also an important—but often overlooked—source of Hg in forest soils. We sampled litterfall at 39 sites in 2003 and 2004 and analyzed the samples for total Hg. The estimated annual deposition of Hg via litterfall in Hadlock Brook watershed (10.1 $\mu g/m^2$) and Cadillac Brook watershed (10.0 $\mu g/m^2$) was greater than precipitation Hg deposition and similar to or greater than the magnitude of Hg deposition via throughfall in these calibrated watersheds. **These results demonstrate that litterfall Hg flux to forested landscapes is at least as important as precipitation Hg inputs.**

Mercury flux was not significantly different among vegetation classes, because less mass of litter counteracted higher Hg concentration in litter at softwood sites. As with throughfall, landscape characteristics (i.e., aspect, elevation and canopy density) were significantly, but weakly, correlated with litter Hg concentrations and flux. The confounding effects of simultaneous differences in landscape characteristics and vegetation types obscured our ability to draw conclusions about direct linkages from this study. What does emerge from these analyses, however, is the predominant effect of vegetation characteristics on Hg dynamics in these managed landscapes.

The proximity of Acadia to the coast, and the fact that winds often originate from the open ocean to the south rather than west, likely also plays an important role in Hg deposition at Acadia. Also, since this study site has the greatest relief along the entire east coast, it is impacted by coastal fog and clouds. Cloud water Hg concentrations are often much higher than the concentration of Hg in precipitation. Research on Hg in coastal fog, and documentation of its frequency and spatial distribution, would provide useful insights to understand Hg cycling at ANP.

3. Is the ocean an important source of Hg during winter and early spring at Acadia National Park?
We further explored the influence of the ocean on deposition at Acadia using seasonal patterns of chloride (Cl), SO_4, and Hg deposition. Although air masses generally track from west to east in summer, many winter storms track northeast along the Atlantic coast in winter. Monitoring at Acadia shows that significantly more sea salt is deposited in winter, possibly due to this seasonal shift in general weather patterns and storm type. Using data from the National Atmospheric Deposition Program and Mercury Deposition Network, we compared annual wet deposition patterns in Maine with other regions. **Seasonal patterns of Cl and the ratio of SO_4:Cl in wet deposition show that in winter, air masses track over the ocean before reaching Acadia**

National Park. Hg and SO_4 wet deposition are greatest in summer and least in winter, while Cl deposition is greatest in winter and least in summer. Initial results from snow throughfall collection in winter 2004/5, immediately following the throughfall season for this research, indicate that throughfall deposition of marine aerosols is also greater in winter than summer. This seasonal pattern provides a starting point by which to model deposition year round at Acadia.

Winter precipitation was far greater in Maine than at the other sites we evaluated in South Carolina and Wisconsin, partly explaining higher Hg deposition. **Winter Hg deposition for Acadia could represent as much as 27.5% of annual flux**, and winter and spring Hg flux combined was 65% and 57% of annual flux for the non-drought years. More study is required to determine whether—and how—marine storms contribute marine-derived Hg to ecosystems at Acadia.

4. Do the patterns of atmospheric deposition correlate with water chemistry?

One of the goals of this project was to evaluate whether there was any correlation between "hotspots" of atmospheric deposition and water quality impairment. With SO_4 and Hg deposition maps created using throughfall and model data, we conducted a park-wide stream survey and coordinated stream water quality data from the last 20 years into a single database.

We sampled 28 stream sites during a one-day coordinated stream survey. We selected stream sites with the widest range of chemical conditions and landscape positions, as well as sites that were sampled in the past. Equilibrated pH values were between 6.4 and 7.6, except for Hodgdon Brook and Steward Brook, which were both approximately 4.7. DOC ranged from 0.9 to 23 mg/L, with an average of 6.1 mg/L. Total Hg concentration ranged from below the analytical detection limit (0.4 ng/L) to 6.49 in Squid Cove Brook. Oak Hill Stream also had high Hg, 6.26 ng/L, and high DOC, 25 mg/L. Oak Hill Stream and Squid Cove Brook are located in the northwest quadrant of Mount Desert Island. Oak Hill Stream drains a large wetland area and was sampled at the wetland outlet. Squid Cove Brook also drains a small wetland, but it is located farther upstream from the sample site.

For SO_4, the model depends on canopy openness, elevation, and aspect. The model shows highest SO_4 deposition on a few mountaintops, and moderate deposition across the park, especially on the western and southern portions of Mount Desert Island, roughly the un-burned area. Eastern sections of the island and rocky, bald summit mountains have low modeled deposition. Overall, **streamwater SO_4 concentrations followed the deposition pattern,** with the highest values in western and southern sections, especially clustering around Hadlock Pond, its watershed, and the western mountains. Lower SO_4 values were located in the burned zone, and northwest quadrant of the island.

For Hg, the model is more simplistic and depends only on canopy openness, resulting in only two deposition estimates: high versus low deposition. High Hg deposition areas were roughly the same as for SO_4: high elevation areas and moderate deposition across the Park, especially on the western and southern portions of Mount Desert Island. Streamwater Hg values did not follow this pattern, with the highest values in the more lowland-wetland northwest quadrant of the island. The lowest streamwater concentrations for both SO_4 and Hg were typically in the burned

area of the Park, near Cadillac Brook watershed and the Kebo Brook areas. **While there was a relationship between SO_4 deposited from the atmosphere and surface water chemistry, the relationship between Hg deposition and stream water concentration was more complex.**

The results of the stream survey collected as part of this project were included in a database of over 1,200 observations for streamwater chemistry at Acadia National Park, spanning a time period from 1982-2004. Most of the samples in the database include full ion chemistry, and 161 include data for Hg. The database has been submitted to the National Park Service, and the data have also been transferred to www.pearl.maine.edu, the source for freshwater environmental information in Maine. This online data library is publicly available for use by researchers, agency staff, students and educators. We have also created a GIS layer of all of sample sites, indexed by project name.

Implications

Research sites like the Hubbard Brook Experimental Forest in New Hampshire and the Bear Brook Watershed in Maine have proven the value of long-term watershed-scale data collection. With the results of the current study, Acadia National Park now joins a network of established watershed research sites. The pair of gauged catchments established in late 1998 provided the foundation for research on the status and trends of Acadia's ecosystems, which were representative of coastal New England. Together, results from studies at these different locations provide managers with regional indicators and models.

This research provided a continuous (1999-2005) record of streamwater chemistry and fluxes for paired watersheds at Acadia National Park, making the site one of the most intensively studied for Hg in the U.S. The Acadia watersheds are part of the Northeast Ecosystems Research Collaborative, which focuses on coordinating regional data summaries and assessments. A key factor in Acadia’s usefulness to collaborators is open data accessibility. The first six years of gauged watershed research produced 22 papers by 29 different authors, funded by eight grants. The core baseline data have been maintained in a centralized database and portions of it are available at www.pearl.maine.edu.

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1. Introduction

1.1. Problem Statement

Acadia National Park (ANP) is a designated Class I area by federal Clean Air Act regulations (40 CFR §52.21). Class I designation affords Acadia National Park the highest degree of air quality protection. Acadia's steep slopes, high peaks, and proximity to coastal fog create an environment conducive to the interception of polluted air masses (Weathers *et al.* 1986). Therefore, an issue of particular importance at Acadia is long-range transport of atmospheric contaminants, including toxic trace substances such as trace metals (Kahl *et al.*, 2000; Norton *et al.*, 1997), persistent organic substances (Matz, 1998), mercury (Hg) (Stafford and Haines, 1997) and acidic deposition (Kahl *et al.*, 2000; 1992; 1985). The input of acids and Hg *via* wet deposition is well characterized at Acadia, based on data from the National Atmospheric Deposition Program (NADP) since 1980, and the Mercury Deposition Network (MDN) since 1995. In the 1980s, fog pH was frequently documented below 3.5 (Jagels, 1989; Weathers *et al.*, 1988).

Elevated deposition of contaminants, including Hg, has been documented at Acadia (Norton *et al.*, 1997). Kahl *et al.* (1992; 1985) and Heath *et al.* (1992) documented acidic episodes in streams, with pH values as low as 4.7. Nitrate (NO_3) concentrations in several streams are chronically elevated (Nelson *et al.*, in press), a condition that suggests nitrogen (N) saturation of these forested watersheds (Aber *et al.*, 1998). Longcore *et al.* (in press) documented that tree swallow chicks and eggs from areas of Acadia are at least as contaminated with Hg as birds living at a Hg-contaminated Superfund site in Massachusetts.

This project built on prior research in paired calibrated watersheds at Acadia, which provided a context of landscape contrasts, and watershed mass balance data that established a conceptual framework. This project provided an estimate of deposition to the entire Park, based on the small watershed results, that takes into account the effects of enhancement due to landscape factors. Further, this project established that there is a relationship between sulfate (SO_4) deposited from the atmosphere and surface water chemistry, and that this relationship does not translate directly to Hg.

Hg and major ion deposition to the landscape are typically evaluated using wet-only precipitation data. Differences in watershed and vegetation characteristics control the input of water and major ions to these watersheds because vegetation type influences throughfall chemical and hydrologic inputs (e.g., Houle *et al.*, 1999; Lovett *et al.*, 1996; Cronan and Reiners, 1983). At coniferous sites, the greater scavenging efficiency and year-round foliage resulted in greater SO_4^{2-}, Cl^-, and Na^+ concentrations and lower pH in throughfall at Hadlock Brook watershed (Nelson, 2002). Throughfall SO_4^{2-} was two- to three-times wet deposition, in the range reported for SO_4^{2-} for the Bear Brook Watershed in Maine (Rustad *et al.*, 1994). Because dry deposition of Hg and conservative ions can equal or exceed wet deposition, we have measured throughfall as a better estimate of deposition, and estimated the flux of Hg as litterfall (Sheehan, 2005). Litterfall Hg flux was similar in magnitude to throughfall deposition in these calibrated watersheds. To complete the annual input budget for Hg and major ions, related research in the watersheds is quantifying winter throughfall deposition (Nelson, 2005, in progress).

1.2. Background

Concern over ecological issues such as acidification and Hg bioaccumulation led to the recommendation for permanent long-term ecological research using two gauged-watersheds at Acadia (Kahl *et al.*, 2000)(Figure 1). PRIMENet (Park Research and Intensive Monitoring of Ecosystems Network) was a joint U.S. Environmental Protection Agency and National Park Service program established in the late 1990s to assess the effects of environmental stressors on ecological systems nationwide. The network of 14 monitoring and research sites used Park units as outdoor laboratories, where environmental changes are monitored in relatively undisturbed and protected sites (http://www.forestry.umt.edu/research/MFCES/programs/primenet/).

The initial focus of the PRIMENet project was atmospheric deposition of N and Hg, and their ecological consequences. Previous funding at these sites has provided data on the paleo-history and current status of forests (Schauffler *et al.*, in press; Wiersma *et al.*, in press), soil pools of Hg, N, and carbon (C) (Kahl *et al.*, in press; Amirbahman *et al.*, 2004), N-status of the watersheds (Nelson *et al.*, in press; Campbell *et al.*, 2004), and throughfall deposition of Hg (Johnson *et al.*, in press; Johnson, 2002), major ions and acidity (Nelson, 2002). Complementary research in the Park has evaluated soil N and C status (Parker *et al.*, 2002; 2001), throughfall deposition of Hg and major ions in snow and snowpack (Nelson, in progress), Hg in birds (Longcore *et al.*, 2 papers, in press) and salamanders (Bank, 2005), as well as a comprehensive review of Hg in the Park's biota (Bank *et al.*, in press). The wealth of baseline and characterization data enhances the value and interpretation of results from this project, though its focus is specifically the stream chemistry and throughfall components of this watershed research.

The throughfall approach for investigating watershed processes allows investigators to assess the effects of heterogeneity inherent in forested, mountainous areas with diverse, often patchy land use histories (Weathers *et al.*, 2000). Throughfall is precipitation that falls though the forest canopy. Research by Nelson (2002) and Johnson (2002; in press) has determined the factors that control throughfall flux of Hg, SO_4, NO_3, and other major ions in the two gauged research watersheds. The two research watersheds were sampled intensively for landscape controls on throughfall inputs from over 32 and 47 hectares in area, respectively (Figure 2). In complementary research, Weathers *et al.* (1998; 2006) estimated deposition of sulfur (S) and N over more than 9,000 hectares of the Park using a coarser grid of sampling (Figure 3).

1.3. Objectives

This research focused on quantifying the influences of landscape factors on throughfall chemical flux, linking estimates of atmospheric deposition with stream water flux and spatial patterns in stream chemistry, and evaluating the magnitude of the deposition flux of Hg *via* litterfall. The key analytes for modeling were SO_4, a link between the work of Weathers *et al.* and this project, and Hg, an element studied more intensely in these watersheds than perhaps any other location in the US. Though these two substances were focal points, all samples were analyzed for full ion chemistry and are presented in the digital appendices. The project continued the long-term monitoring component with watershed measurements and mass balance calculations. Specifically, the objectives were to:

1) Continue the PRIMENet intensive watershed monitoring for stream chemistry and flow to enable calculation of elemental mass balances [Section 3.1].

2) Compare and contrast the Weathers *et al.* park-scale deposition map for S and N deposition to our intensive small watershed throughfall data [Section 3.2].

3) Scale the deposition model for S to the entire Park for other analytes, especially Hg [Section 3.3, Section 3.4]. We also evaluate the importance of litterfall Hg deposition [Section 3.7].

4) Use a field season of stream chemistry to determine whether modeled deposition loading translated directly to stream water quality. A corollary objective was to coordinate legacy datasets into an Acadia stream chemistry database. This database provided background data for this study and was transferred to the Park and to web-based data repositories to enhance access [Section 3.5, Section 3.6].

5) Though not an original proposed objective, each research watershed and individual site was logged with a GPS unit and translated into GIS (Geographic Information Systems) layers that contained detailed site characteristics. Sampling points from legacy datasets – previously only available on a single hard-copy map – were also hand-digitized and migrated to GIS. These data were transferred to the NPS at Acadia for future use by other researchers [Section 2.8, Section 3.6].

A major focus of this research project was Hg. The deposition of atmospheric Hg is an environmental and human health issue in northeastern North America, where the complexities of total deposition (wet, dry and occult (cloud and fog deposition)) are poorly characterized by wet-only deposition (1, 2). In this region, dry deposition (particles and gases in air masses) of Hg equal or exceed wet deposition (Hg in rain and snow), and is likely the largest vector of Hg input from the atmosphere to terrestrial ecosystems (Grigal, 2002; Miller *et al.*, 2005). Forest cover enhances Hg deposition because forests act as filters, scavenging dry Hg from air masses (Lindberg *et al.*, 1994; Rea *et al.*, 2000). The Hg deposited on forest canopies is subsequently washed by precipitation as throughfall to the forest floor.

Total mercury deposition is of particular concern at ANP, despite the Park's Class I air quality designation and distance from major emission sources. Many of the Park's biota contain elevated concentrations of Hg (Bank *et al.*, in press). Mercury concentrations in ANP tree swallow (*Tachycineta bicolor*) feathers and food boluses have been documented to exceed concentrations measured at a Massachusetts Superfund site (Longcore *et al*., in press). Smallmouth bass (*Micropterus dolomieu*) collected in ANP had mean Hg concentrations more than twice the state average for the species (Bank *et al.*, in press; Burgess, 1997). This research provides further evidence that total Hg deposition is elevated in Acadia National Park, and begins to identify landscape characteristics (coniferous forest types, high elevations) where deposition hotspots may occur.

1.4. Funding Report

This project continued support for watershed deposition and stream measurements originally funded by US EPA-PRIMENet, and supported specific new research that was often integrated with research supported by other contracts and investigators. Several spin-off projects were developed to more fully investigate specific research questions such as the role of snow deposition in total Hg deposition estimates. The following is a list of project tasks directly funded by this research contract:

- Cadillac and Hadlock Brook stream chemistry sampling, USGS discharge monitoring, flux calculations for water years 2002 - 2004.
- Throughfall (rain) site selection via cluster analysis and throughfall sampling, 2004.
- Statistical analyses of 2004 throughfall data.
- Comparison of Weathers et al. LANDMod model to data collected in paired watersheds.
- Development of CART model for S and Hg deposition across MDI.
- Island-wide stream survey sampling and analysis for major ions and Hg, 2004.
- Comparison of Hg and S deposition model to stream survey results.
- Compilation of streams database for Acadia National Park, including available legacy data from 1982-2004.
- Development of GIS layers for each sample site and watershed.
- Litterfall mercury study (plus supplemental funding from other sources).

Several projects provided additional data and context for this research, though not funded by NPS. Following is a list of tasks funded through other funding sources, which provided value-added information to the project:

- Development of LANDMod atmospheric deposition model (Weathers et al.).
- Litterfall mercury study (Fernandez et al).
- Winter deposition study and seasonal patterns investigation (Nelson et al.)

The PRIMENet project and supplemental funding from USGS-BRD, University of Maine, and other sources funded all research in the study watersheds between 1999-2001.

2. Methods

2.1. Site Descriptions

Acadia National Park is located at the temperate and boreal transition zone in North America. Its coastal location and prominent topography result in frequent cloud and fog cover. Mean annual daytime temperature for Bar Harbor, Maine is 13° C and mean annual nighttime temperature is 2° C (Acadia National Park Official Website, www.nps.gov/acad). Prevalent wind direction at Bar Harbor is 220° to 240° (west-southwest; Zielinski, pers. comm.). Average annual precipitation for Acadia is 122 cm as rain, plus 155 cm as snow near park headquarters (Table 1), for an average wet total of 137 cm. Seasonal precipitation is relatively evenly distributed, with minimum values occurring in summer and the highest monthly amount in November (Table 1).

Under US EPA and USGS funding in 1998, two gauged watersheds were established: Cadillac Brook watershed and Hadlock Brook watershed (Figure 2). Reconstructed forest stand histories based on pollen and charcoal analysis document major vegetation and disturbance differences in Hadlock and Cadillac watershed forests during the last several centuries (Schauffler *et al.*, in press). The pollen data indicate that Hadlock Brook watershed has not burned or been significantly cleared for 500 years or more. Most of Cadillac Brook watershed burned in an intense wildfire that covered over half of the Park in 1947, and likely burned several times in the 1800s. The pollen data suggest that Cadillac Brook watershed has supported a heterogeneous forest for 200 years or more. The two sites are representative of the two major forest types located in the park: those that burned in 1947, and those that are undisturbed spruce-fir. In addition, the sites were selected for this research because of the long-term data record, existing instrumentation, and detailed site characterization.

Cadillac watershed is drained by headwater Cadillac Brook. The gauging station for this burned watershed is located at latitude 44°20'41.0", longitude 68°13'01.5" (NAD 27) (Figure 2a) at an elevation of 122 m. The watershed area is 31.6 ha, extending from the summit of Cadillac Mountain (468m) to 122m above sea level. The average slope is 28%, with an east-southeast aspect. The stream begins at about 440 m in a small valley, descends through open bedrock sections *via* multiple small drainage channels and overland flow, and converges in the bottom third of the watershed.

The Hadlock watershed is drained by a headwater stream called Hadlock Brook. The gauging station for this unburned reference watershed is located at latitude 44°19'54.0", longitude 68°16'47.5" (NAD27) (Figure 2b) at 137m above sea level. The watershed area is 47.2 ha, extending from the summit of Penobscot Mountain (380m) to 137 m. The average slope is 21%, with a generally southwestern aspect. The stream headwaters are in a 0.7-ha woodland bog/fen at the north end, descending through a mature spruce-fir forest until reaching the gauging station.

2.1.1. Site Selection for TF

Throughfall was first measured at these sites during 1999-2001. This project continued monitoring throughfall, and due to our understanding gained during previous research, used fewer collection sites. A simultaneous snow study utilized fewer sites than throughfall due to the

logistical challenges of winter access. Overall, there were up to 80 individual throughfall sites sampled in the first three years (1999-2001) of the watershed research program, which were then reduced to 21 sites for the project reported here (Figure 4). For snow, a project funded by other sources, 12 sites were selected. Selected sites represent the range of landscape and chemical conditions that were measured during 1999-2001.

We used cluster analysis to statistically select sites for this research, and to recommend sites for periodic re-sampling of throughfall deposition. Cluster analysis is a multivariate statistical technique that groups observations in order to minimize within-group variability, and between-group variability is maximized. The technique is purely exploratory, and thus there are no assumptions that must be met to use cluster analysis. Both continuous and discrete data can be used, a benefit for this type of landscape-chemical dataset. Determination of specific cluster distances and methods to use is somewhat subjective, and requires inspection and comparison of cluster trees. For this purpose - site selection - where the number of clusters desired is known *a priori* and multiple methods agreed well, the technique is appropriate.

We selected four individual throughfall events for cluster analysis to avoid repeated measures issues with landscape variables. The final collections analyzed were numbers 6 (November 1999), 7 (May 2000), 11 (July 2000) and 14 (October 2000). We evaluated mean values from each of these collections as compared to the overall mean to ensure that these selections represented the range of chemical (conductivity and Hg), seasonal, and rainfall conditions observed in the field.

For this study, the desired number of clusters was known *a priori*: ~20 for one purpose (rain-throughfall study) and ~10 for another (snow study). Both K-means and hierarchical clustering methods were used and results compared. Number of clusters (10 or 20) is hereafter referred to as 'level'. The final result was therefore 16 cluster analyses (4 collections x 2 levels X 2 methods). Each analysis provides a dendrogram showing clusters of sites (e.g., Figure 5). Each cluster was, effectively, a list of sites that were the most similar with respect to chemistry, water input, and landscape factors.

Results were similar between the K-means and the hierarchical cluster analyses. To select the sites to be sampled for this study, we compared across analyses to choose sites that were representative in each of the 10 or 20 clusters. Within a given cluster, sites were selected using the following criteria: 1) sites were preferred that had been sampled continuously in 1999-2001; 2) more field-accessible sites were selected (especially for snow collection); 3) a similar number of sites were selected in each watershed; and 4) the "PARKB" site (co-located at the McFarland Hill NADP/MDN site) was retained as it is located outside the watersheds and allows comparability with other studies. The final sites that were selected are shown in Figure 4.

Cluster analysis is an exploratory tool, and worked well in assessing the similarity among these throughfall observations. Principal components analysis after clustering indicated that chemical variables were intertwined, and gradients in vegetation characteristics and elevation were important influences on chemistry, confirming earlier univariate statistical results (Johnson, 2002; Nelson, 2002) and relationships in the literature (e.g., Weathers *et al.*, 2000; Lovett *et al.*, 1999).

2.1.2. Weathers *et al.* Empirical Modeling Study

Weathers *et al.* modeled deposition to the park landscape using throughfall S data collected from 300+ locations within the park (Weathers *et al.*, in revision; see also Weathers *et al.* report to NPS). Area-weighted S and N deposition were found to be 50 and 70% greater than NADP + CASTNET estimates for the McFarland Hill location. Validation exercises suggested that the empirical model, LANDMod, overestimated deposition at low elevations (also regions of low deposition) and underestimated deposition at high elevations (also regions of high deposition). A resin throughfall method was also developed as a result of this research (Simkin *et al.* 2003). The LANDMod will be further evaluated and compared to the two-watershed analysis described in this report.

2.1.3. Site Selection for Streams Survey

We proposed that the deposition maps could identify 'hotspots' of deposition (Weathers *et al.* 2000, in revision). We further suggested that, by sampling a subset of streams draining small watersheds at the end members of the spectrum of deposition, we could correlate or de-couple inputs from streamwater concentrations, and thus identify landscape controls for further investigation. Several streams were selected in the types of terrain predicted to have the lowest deposition, and several were selected in the types of terrain predicted to have the highest deposition. We used a cluster analysis similar to that used for throughfall site selection, weighted by completeness and length of data record, to determine which stream sites in the Park to sample for the stream survey. We selected 30 sites draining watersheds at high and low elevations, and with varying vegetation composition, for a one-day coordinated sampling effort (Figure 6). This sampling had the added purpose of providing data on a population of streams, some of which had not been re-surveyed since 1984 (Kahl *et al.*, 1985).

2.1.4. Litterfall Sites

Litterfall was sampled at a total of 19 sites in Hadlock Brook watershed and 20 sites in Cadillac Brook watershed (Figure 7). The network of 39 sites consisted of: (1) 12 core sites used for long-term sampling of litter, throughfall, and soil (Amirbahman *et al.*, 2004; Johnson, 2002; Nelson, 2002) for the PRIMENet study, (2) 17 throughfall study sites located along transects from throughfall studies (Nelson, 2002), and (3) 10 additional sites randomly located within under-represented vegetation types. Some of the original throughfall transect study sites were omitted because they either over-represented a vegetation type, or were not located beneath a vegetative canopy. The study sites chosen provided both a balance of replication within major vegetation types to the extent possible while linking this research to other ongoing studies in these watersheds (Figure 2). At each site, measurements of aspect, canopy cover, and elevation were conducted as described by Sheehan (2005).

2.2. Environmental Planning/Permits

Each year of the project, the research team received National Park Service permits and completed an Investigator's Annual Report. Permits varied by year to reflect specific activities

such as throughfall and litterfall sampling, which were additions to the baseline streamwater monitoring activities.

2.3. Field Methods

2.3.1. Calibrated Watershed Stream Sampling

Streamwater grab samples were collected from Cadillac and Hadlock Brooks weekly in the spring and fall and bi-weekly or less in the summer and winter. These samples were analyzed for complete laboratory analyses, using standard EPA stream sampling procedures (Kahl *et al.*, 1992; Peck *et al.*, 1993), including semi-clean collection methods for total Hg modified from EPA Ultraclean method 1669 (Johnson, 2002; Louch, 2003). Stream samples were taken from small pools in the main stream channel just upstream from the USGS gauging stations for each watershed. Samples for Hg analyses were collected in 500 mL Teflon™ bottles. Major ion samples were collected in HDPE bottles and syringes. Duplicate samples were collected on an alternating watershed schedule.

Event sampling occurred when flow exceeded ~1 cfs in Cadillac Brook and ~2 cfs in Hadlock Brook. ISCO™ auto samplers collected one sample every four to 12 hours (depending on our advance programming) until stream flow decreased to below the threshold. Event samples were collected in borosilicate glass for Hg samples and in HDPE bottles when Hg analysis was not performed. Automated ISCO samplers were used beginning in 2000 for event sampling for full chemistry, except closed-cell pH and dissolved inorganic carbon, which have short holding times and thus require manual sampling. Hg was collected only in non-freezing season events because ISCO sample containers for Hg are glass. Streamwater samples have not been taken during dry periods, such as the drought which dried up both streams in much of 2002, or during severe freeze-up, such as the winter of 2003-2004, when up to four feet of ice was observed for over a month on Hadlock Brook.

2.3.2. Stream Sampling – Survey

Twelve staff and students from the Mitchell Center, with support from Acadia National Park Resource Management, carried out the island-wide stream survey in an eight-hour period on October 6, 2004. Grab samples were taken using the same methods and equipment as in calibrated watershed streamwater sampling. GPS points and photographs were taken at most of the sites to assist with the mapping effort. Two sites with very small streams did not have adequate flow for sampling at the time, despite a generally wet summer and fall. Duplicate samples for major ions and Hg were taken at 10% of the sites for quality control/quality assurance purposes.

2.3.3. Throughfall

Funnel-bottle throughfall collectors were based on the design of Lawrence and Fernandez (1993) and were placed at a height of one meter above the ground, using schedule 80 PVC pipe as a support structure (Figure 8). Funnels were 16 cm diameter, and sample bottles were 1-L capacity. Each throughfall collector had two funnel-bottle units: one for Hg sample collection

(hereafter, 'Hg TF collector'), and one for major ion and other analyte sample collection (hereafter 'TF collector'). All components of the TF collector were Nalgene high-density polyethylene (HDPE). Components of the Hg TF collector were Teflon (a custom-fabricated, form-fitted Teflon funnel liner and Teflon tubing), Kynar (fittings to connect components), or glass (sample bottles)(Johnson, 2002). A de-ionized water (DI) rinsed poly-wool plug was inserted into the neck of each TF collector funnel and a sialized glass wool plug was inserted in the Hg TF collector funnel to exclude insect debris and plant litter from the collection bottle (Weathers *et al.*, 2001). In both collectors, tubing was half-looped to minimize evaporation. Both collectors had a vent tube with a 0.2 mm hole for Hg TF, 0.5 mm hole for TF, to allow pressure to escape and keep containers from exploding due to temperature changes. The TF collector had an additional 3-L HDPE bottle placed on the ground and attached by a Nalgene tube to the main sample bottle; this was called the 'overflow' container and was used to record the volume of sample if the primary sample bottle over-filled in large rainstorms. This overflow volume was applied to both the TF and Hg TF sample volume at the same collector.

All components of the TF collectors were rinsed with hot water, rinsed three times with de-ionized water, and soaked overnight in de-ionized water. The overnight rinse was tested for conductivity for at least 10% of collector components and sample containers, and was required to be <2.0 μs/cm, or containers were soaked another 24 hours and re-tested. Finally, de-ionized water was poured through the TF collector in the laboratory and the resultant laboratory equipment blank was analyzed to ensure that the entire collector was clean.

For Hg TF collectors, all preparation was done in a clean room. Teflon funnel liners and glass wool were rinsed with Aqua Regia then rinsed six times with ultrapure de-ionized water. Small components (collector lids, valves, and connectors) were soaked overnight in Aqua Regia, and then rinsed six times with ultrapure de-ionized water. Teflon tubing was rinsed several minutes with ultrapure de-ionized water. Revision E of EPA Method 1631 allows for generic glass bottles to be used for sample collection, as long as they meet the bottle blank criterion (Louch, 2003). Louch (2003) recommends Class 200 clean bottles, and also notes that bottles need not be filled with acidified water but can be filled with ultrapure de-ionized water or left empty before deployment in the field (Louch, 2003). For throughfall sampling, Class 200 amber glass bottles were rinsed three times, filled with ultrapure de-ionized water, and double bagged for transport to the field. Results for laboratory and bag/bottle blanks were required to be less than the detection limit for the Tekran Hg analyzer (Appendix A). Gloves to be used for sample collection were bagged in individual zipper-seal bags in the clean room.

Two field crews collected throughfall solutions simultaneously in both watersheds after a volume of 500-1000 mL (equivalent to depths of 2.55-5.10 cm) of precipitation had accumulated, typically every two to three weeks. For N species, collection intervals of two weeks or more with unpreserved samples may result in biased or unreliable data. Due to the study location in a National Park, it was not feasible to pre-acidify sample containers in the field; therefore, N results from biologically active compounds have a large potential error. All sites were accessed on foot, and were >1 km from paved roads, except at the Cadillac summit, where sites were >130 m (Cadillac summit) from roads. The McFarland Hill bulk collector site met the NADP site location criteria, >100 m from parking areas. The throughfall collection procedure is detailed in Appendix B.

TF collectors were rinsed in the field with 350 mL of de-ionized water between sampling periods; Hg TF collectors were rinsed with 1 L of ultrapure de-ionized water between sampling periods. Samples were iced at the vehicle and returned to the laboratory within two hours, where they were refrigerated until processing; Hg TF samples were refrigerated until preserved with bromine monochloride (BrCl) in the sample bottle within 28 days of receipt at the laboratory.

2.3.4. Litterfall

Litterfall was collected in polyethylene basins, and unsorted dried samples were analyzed for total Hg, using a modification of EPA method 245.6 (*Determination of Mercury in Tissue*), by cold vapor atomic absorption (Sheehan, 2005). A sub-set of samples were analyzed for total-C and total-N with a LECO CN Analyzer (Sheehan, 2005).

2.3.5. Snow Throughfall

The snow throughfall study was supported by separate funding for the period 2004-06. Snow throughfall sampling methods were analogous to those for rain throughfall sampling. Snow throughfall inputs will be used to complete the mass balances in 2006 and validate previous estimates of winter deposition.

2.3.6. Hg – Special Considerations

Because Hg is typically found at parts per trillion (ppt) levels and samples are easily contaminated, Hg research requires special field sampling techniques. For Hg sampling in the field, US EPA recommends: 1) wearing pre-cleaned and clean-bagged windsuits; 2) double bagging all sample containers and apparatus; 3) using the 'clean hands-dirty hands' technique, where only the 'clean hands' technician contacts the sample container and inner bag; 4) wearing non-talc, vinyl gloves (shoulder-length for the 'clean hands' person); and 5) approaching the sample site from down-current and downwind (EPA Method 1669, 1996). For this research, a performance-based field method (hereafter, 'semi-clean' technique) has been used to streamline the recommended sampling procedure (Johnson, 2002; Louch, 2003). Field technicians wore non-talc gloves, and used the 'clean-hands, dirty-hands' technique and samples were double bagged before deployment and at collection, but windsuits and shoulder-length gloves were not worn, and a downwind approach was not always taken due to site location; a downstream approach was taken. The semi-clean methodology produced results that were not significantly different than those obtained using the stricter methodology in replicate samples (Johnson, 2002; Louch, 2003).

Field quality control (QC) samples for this research consisted of field duplicate samples, field equipment blanks, sampling equipment blanks, and pre-deployment bottle or bag blanks, as appropriate for a given sample type (e.g., it is not possible to take a duplicate sample for throughfall, and an equipment blank is irrelevant for streamwater grab sampling)(Appendix A). When Hg TF collectors were deployed in the field, they were rinsed with ultrapure de-ionized water and the final 250 mL of rinse water was collected and analyzed as an equipment blank. Equipment blanks did not have significantly higher Hg concentrations than field blanks or did

not exceed two times the method detection limit for the 1999-2000 Hg TF data (Johnson, 2002) or for this project period (Appendix A).

2.4. Discharge Monitoring by USGS

The U.S. Geological Survey, in Augusta, Maine, monitors stream stage at the outflow of each watershed with a pressure transducer linked to the World Wide Web via satellite (http://waterdata.usgs.gov/me/nwis/). Streams were instrumented at sites with suitable natural bedrock control of the stream channel, with USGS stage recorders that recorded stage at five-minute intervals. Stage was used to calculate streamflow in each stream based on stage relationships and the stream profile (Table 2). Stream discharge was greatest in spring and fall and typically low in summer (Figure 9).

2.5. Precipitation Monitoring by NADP/MDN

The National Atmospheric Deposition Program/Mercury Deposition Network, in collaboration with the National Park Service, monitors wet-only precipitation at site ME98, McFarland Hill, in Acadia National Park (Figure 1). For each deposition study as part of this research, we have co-located a collector at the McFarland Hill site. The data from these collectors have been used to compare results from the various studies and to compare to wet-only deposition. Simkin *et al.* (2004) reported 3.16 and 4.04 kg/ha S deposition at their two collectors at McFarland Hill, while our co-located collector measured 4.04 kg/ha (Simkin *et al.*, 2004) and the NADP reports 3.20 kg/ha for the comparison period in 2000. For Hg, Johnson (2002) reported 2.2 ug/m^2 for June 1 – November 15, 2000, and the MDN site indicates 3.1 ug/m^2 for the same collection period.

2.6. Input Budget Calculation

Throughfall data were collected in 1999-2001 and 2004, plus winter/early spring collections were made in 2004/2005. Throughfall flux was calculated from the measured data for each water year, for comparison to NADP wet-only data and as inputs to mass balances. For each collection and location, deposition was calculated based on the depth of precipitation (determined from volume), catch area of the funnel, and chemistry data. Fluxes were spatially weighted by vegetation type as mapped by the USGS-NPS vegetation mapping project (Figure 2; Lubinski *et al.*, 2003) to calculate deposition to the entire watershed per unit time (e.g., Nelson, 2002). For winter periods when throughfall was not collected, we used the NADP or MDN deposition values, conservative estimates of deposition.

Comparison with Weathers et al. deposition map (ongoing). To compare results of this research to that of Weathers et al., throughfall flux had to be calculated for each individual site. First, sites with a complete record during June 1 – September 30, 2000 were selected. Then, deposition was calculated as above. Deposition was then summed for the period for each collector. Finally, deposition was annualized by multiplying by the fraction of the year represented. These values, in units of mass/area/year are being used to compare between the two studies. The annualized values do not represent estimates of annual deposition, but simply provide a standardized unit by which to compare between the two studies.

For litterfall, differences among means by vegetation type were assessed for statistical significance by Analysis of Variance (ANOVA) at a 95% confidence level. Continuous data sets (elevation, canopy cover, and openness) were tested for significance of correlations with litterfall, litter Hg concentration, and Hg flux in litter. A modified ANOVA, utilizing contrasts, was used to test for interactions among landscape factors whenever possible. All means are reported with their corresponding standard error (± SE). Time-weighted mean litterfall and mean litter Hg flux values are reported to account for differences in the length of the collection periods used in this study.

2.7. Laboratory Methods

2.7.1. Major Ions

Throughfall, snow, and streamwater samples were analyzed for major ion chemistry at the laboratories of the Senator George J. Mitchell Center for Environmental and Watershed Research at the University of Maine, using standard methods (Peck *et al.*, 1993; Norton and Fernandez, 1999) in place for more than a decade as part of several major U.S. Environmental Protection Agency (EPA) projects (Appendix C). The laboratory participates in US Geological Survey and Environment Canada audit programs to ensure data quality (Youden, 1969). Laboratory quality control procedures include field and laboratory blanks, replicates, and standards (Appendix D).

Throughfall samples were analyzed for major anions (Cl^-, NO_3^-, SO_4^{2-}), cations (Ca^{2+}, Mg^{2+}, K^+, Na^+, NH_4^+), DOC (dissolved organic carbon), air-equilibrated pH, conductivity and apparent color. Samples with an equilibrated pH greater than 5.5 were analyzed for acid neutralizing capacity (ANC) in order to determine ion balances for quality assurance purposes. Below pH 5.5, ANC is quantitatively unimportant and was not measured. Streamwater samples were analyzed for major anions, cations, DOC (dissolved organic carbon), TIC (total inorganic carbon), closed-cell pH, air-equilibrated pH, conductivity, apparent color, ANC, total aluminum (Al) and organically-bound Al. Estimates of charge contributions for Al and DOC charge were based on Kahl *et al.*, (1989). Data were re-evaluated and/or samples re-analyzed for samples with charge balance discrepancies greater than 10% for streamwater and 15% for throughfall, a tighter guideline than specified by EPA QC protocols (Peck, 1992).

2.7.2. Hg

All samples collected for this project were analyzed for total Hg. Hg analyses were performed by the University of Maine's Sawyer Environmental Chemistry Research Laboratory, the same laboratory that has performed all Hg analyses for these watersheds since 1998. The Laboratory operates a Tekran Model 2600 cold-vapor atomic-fluorescence spectrometer (CVAFS) in a clean room, which allows for the determination of Hg in water samples to 0.5 ng/L (ppt) or lower. The Laboratory has processed thousands of water samples for Hg analysis maintaining quality control levels in excess of the EPA standards set out in EPA method 1631. All water samples were analyzed on the Tekran, adhering to EPA method 1631 (EPA, 2002) for the analysis of Hg in water. Purge techniques used with this instrument differ from those specified in the method, namely that a phase-separator tube is used in place of the bubblers, eliminating foaming in

samples with a high organic carbon concentrations. Laboratory QA/QC results during the course of this project were within EPA recommended limits (Appendix A).

2.7.3. Laboratory Change during this Project

There was a change in laboratories conducting major ion chemistry in 2002. From 1982 to 2000, aquatic-related research at Acadia National Park was overseen in UMaine laboratories by J.S. Kahl. In late 2000, the former Mitchell Center laboratory came under the management of the Civil Engineering Department as a contract laboratory, and is hereafter referred to as the Sawyer Laboratory. In 2002, the Mitchell Center re-established a laboratory dedicated to low ionic strength waters, including acidic deposition-related research. After a period of duplicate analyses between laboratories, and review of audit results for both laboratories during the period of overlap (Appendix E), we are confident that the data provided for this project met QA/QC standards and are the best available data.

2.8. Database & GIS Methods

2.8.1. GIS

With equipment and assistance from Karen Anderson at Acadia National Park, we re-visited the watershed boundaries as flagged in 1998, and marked the boundaries using a GPS, later importing them into a new GIS coverage. The new watershed boundaries were compared to: 1) the older boundaries developed using GPS/GIS; 2) a hand-drawn topographically-derived watershed divide map; and, 3) watershed boundaries modeled using the Arc Hydro module of Arc GIS. Because the original boundaries were not compared to this third data source, it was desirable to do this quality assurance check. The new boundaries were similar to the originally-derived boundaries, and the group settled on final maps for the two watersheds.

We collected additional GIS data for use in this project, specifically the modeling component. We received the newly-released USGS-NPS vegetation map and documentation from the Upper Midwest Environmental Services Center (Lubinski *et al.*, 2003). We obtained other park-specific coverages such as streams, carriage roads, and fire coverage from the National Park Service. Other layers for Mount Desert Island were obtained from the Maine Office of GIS (http://musashi.ogis.state.me.us/).

All sample sites that were part of the original PRIMENet research (soil plots, streamwater gages, AeroChems, and throughfall collectors) plus all sites that were part of this current project were marked with GPS and converted to coverages in GIS (Figure 2). The final coverage can be joined to project-specific attribute tables (such as canopy openness over a given throughfall collector) using the unique site code identifier for each feature. The points which represent throughfall collectors were used in the first phase of modeling to predict S deposition at the small watershed scale.

We used published data reports and internal sampling maps to create a GIS layer of stream sampling sites across the Park with chemistry data from 1982-present (Figure 6). Sampling points were snapped to streams where reported coordinates or GPS points did not match up with

stream lines. Personal interviews with original project PIs and sample crews, comparison with topographic maps, correlation with published landscape feature descriptions, and hard copy sample maps were used to verify sample locations from GPS or hand-digitized points.

All GIS data sets created for this project were projected using UTM NAD 1983, zone 19N, the standard for the National Park Service at Acadia. Basic metadata were created to accompany each layer, and burned to CD for permanent archiving (Appendix F).

2.8.2. Stream Chemistry Database

We coordinated data from Mitchell Center-related research projects to form a core Acadia streams database. We have identified over 1200 observations from streams at Acadia (exclusive of the paired watershed stream sampling) since 1982 (Appendix G; Figure 6). In the case of Heath *et al.* (1993), we digitized data from the final project report, which was not available in digital format. In this integrated database, units and variable names have been standardized to facilitate interpretation, data sharing, and future research.

The first use of this database was site selection for the island-wide survey. Some Hg data were available from 1999-2000 from Peckenham *et al.* (in press), so we were able to ensure that the highest and lowest ranges in streamwater Hg were included. Most of the sites were sampled by Kahl *et al.* in the 1980s, but Kahl's survey did not include a large number of sites on the west side of Mount Desert Island, some of which had the highest Hg concentrations (e.g., Hodgdon Brook; Oak Hill Stream). By coordinating the databases from historical data sets, we were able to use the best available information to choose sites for the survey, and continue data collection at some sites with the longest and most complete data records (e.g., Hadlock, Penobscot, and Gilmore Brooks, sampled in all Mitchell Center research projects at Acadia since 1982).

The Acadia streams database has been submitted to Resource Management (B. Gawley) at Acadia, and will be posted on PEARL, Maine's web site for geo-referenced environmental information. Chemistry data from the paired watershed streams is already available on PEARL, at http://www.pearl.maine.edu/browseglobal.asp. The PEARL site includes links to other types of data for the same watersheds, and detailed metadata. In addition, the database and/or metadata will appear on SPARC, a new web site designed to coordinate information on research catchments in National Parks across the U.S. The database is permanently archived at the Mitchell Center.

2.9. Modeling Methods

2.9.1. Landscape Factors

2.9.1.1. *Summary of existing data.* All of the throughfall sample sites had been characterized as part of earlier research (Nelson, 2002; Johnson, 2002). Briefly, each landscape variable was measured in the field at individual collector sites (e.g., Weathers *et al.*, in revision). Vegetation type was determined by identification to the species level for vegetation types influencing the collector area, defined as a cone extending upwards from the funnel walls, with an apex angle of 75º. Aspect was determined as the topographic fall line for each collector using a liquid-filled

magnetic compass, corrected for true north. Elevation was measured at each throughfall collector site using a temperature-compensated EB833 electronic altimeter, accurate to 5.5 meters. A dial-type aneroid barometer/altimeter was used in tandem with the electronic altimeter to verify measured elevation. Calibration benchmarks for this research were bedrock outcrops at the USGS gauging stations and USGS-marked mountain summits. Elevations were cross-checked by referencing Seal Harbor and Southwest Harbor 7.5' USGS Quadrangles. Burned or unburned status at individual collector sites was determined by paleo-ecological methods (Schauffler *et al.*, in press) and current vegetation composition.

2.9.1.2. *Canopy Coverage.* In the earlier research project, canopy coverage was determined for each collector site using a LI-COR LAI-2000 Plant Canopy Analyzer, and we used 'DIFN' or gap fraction values (LI-COR, Inc., 1992; Davies-Colley and Payne, 1998). The values produced using this method had little variability, and other methods were sought to better quantify canopy coverage. An alternative method is the use of fisheye or hemispherical photography. A fisheye photo is taken at each site, converted to black and white, and the number of open sky versus vegetation-containing pixels is determined by canopy coverage analysis software. The software determines which pixels to include as open or closed based on a threshold value (i.e., a certain value of gray). The method is roughly analogous to a long-used timber cruising procedure that uses a spherical densiometer, or a half-spherical, convex or concave mirrored ball inset into a wooden box, and mirror sections that are open versus closed with vegetation are counted. Sheehan (2005) used a spherical densiometer at these sites.

This project used a Canon Powershot G3 digital camera and fisheye lens to calculate canopy openness. The camera was set at a height of one meter above the forest floor. The camera was then oriented north, leveled, and at least two photos were taken at two light levels, depending on weather. Photos were imported into Adobe Photoshop for format and color conversion. The prepared photos were analyzed using the WINPHOT 5.0 program (ter Steege, 1996), a freeware program that was simple to use with good documentation. Each photo was analyzed individually, and data exported into an ASCII-text format for use with standard database software.

2.9.2. Regression Tree Modeling Approach

The earlier research at these throughfall sites indicated that vegetation type, elevation, and aspect were important drivers for chemical species distribution (see Section 3.2.1.), but traditional statistical methods did not adequately represent some landscape features, such as the varying character of coniferous communities at different elevations. Canopy fisheye photos indicated that Cadillac sites tended to have more open canopies than Hadlock sites, and openness tended to be greater in winter than summer, as expected (Figure 10). Overall, openness ranged from 15% to 100% in summer with a mean of 54%, and 32% to 100% in winter, with a mean of 72%.

Using the new canopy cover data, we re-evaluated controls on throughfall deposition to determine whether a) canopy cover would become an important controlling factor, and b) canopy cover could be used to better predict deposition where canopy structure seemed to be a confounding factor. Regression trees were evaluated as an alternative approach to the modeling problem. Regression trees "explain variation of a single response variable by one or more explanatory variables…The tree is constructed by repeatedly splitting the data, defined by a

simple rule based on a single explanatory variable." (De'ath and Fabricius, 2000). Unlike other multivariate methods, trees allow the same explanatory variable to be evaluated at each level of splitting. Also, trees produce output that is fairly intuitive and easy to interpret with respect to the original data set.

Regression trees were evaluated for two growing seasons, May-November of 2000 and 2001, to determine whether interannual variability would confound results. Models were constructed using three sets of predictor variables: (1) those determined solely from Geographic Information Systems (GIS)-derived data, such as vegetation communities and distribution; (2) those determined from on-site measurement of canopy openness and vegetation type; and, (3) both sets of predictors together.

2.9.3. Model Coordination

In 2004, Weathers and Simkin (IES) met with Nelson and Diamond (GIS specialist, UMaine) at the University of Southern Maine to begin work on comparing data between the Weathers et al. project and this project. The first day of meetings included exchange of chemical and GIS data, identification of the sampling period that overlapped for both studies, and exploration of throughfall data to determine correlation among analytes. As expected for throughfall, lower volume samples had higher concentrations of chemical analytes. Good correlation (Pearson correlation coefficient ~0.7) was found for S and N deposition and concentration, and for S and Hg concentrations in aqueous throughfall samples collected in the Johnson (2002) and Nelson (2002) projects. These analyses indicated that S may be used in the model to predict concentration and/or deposition of other substances.

In ongoing meetings and electronic data exchanges, we have begun to compare the Weathers *et al.* (in revision) empirical model S fluxes and the Nelson (2002) measured flux for the same period in the two study watersheds. We examined several data plots comparing the results, and identified several areas on which to focus the remaining efforts. Our preliminary examination of these data suggested that the Weathers et al. model over predicted S deposition for the aqueous throughfall collectors. Examination of field notes indicated that these sites were dominated by short-stature, wind-blown coniferous woodlands, while the GIS vegetation coverage on which the empirical model is based classified them as coniferous. Thus, one area of focus for the future is to determine how much of the Park area is scrub/shrub vegetation, and how that might affect the empirical model.

In 2004 and 2005, GIS coverages of both sets of throughfall sites were exchanged, as were chemical data sets for both projects. A meeting in June 2005 set tasks for completion of the project and coordination of the small watershed and whole-island approaches.

2.9.4. Scaling to Other Time Periods: Seasonal Deposition Patterns

Wet-only loading of sodium (Na) and chloride (Cl) is highest in winter at Acadia (National Atmospheric Deposition Program, 2003), a result of the dominant coastal storm track. In summer, most precipitation is from convective storms tracking across inland regions. The same pattern of higher winter deposition of marine-derived substances occurred in Hiroshima, Japan,

where winter storms originated from marine sources (Seto *et al.*, 2000). Because of its proximity to the ocean and the marine origin of some SO_4, Acadia National Park has received 20% to 40% more SO_4 in wet deposition annually than inland sites in Maine for 1997-2001 (NADP, 2003).

We repeated an analysis of wet-only precipitation data conducted by Mason *et al.* (2000), in which data from three MDN sites were used to analyze seasonal deposition patterns. Our variation on this analysis was to include Acadia, since the Mason *et al.* analysis focused on the Mid-Atlantic and Midwest; anecdotal evidence suggested that Acadia's patterns may be quite different. We compared deposition of Hg, Cl, and SO_4 at three NADP/MDN sites, including Acadia, to determine seasonal patterns of deposition. Cl and the SO_4 to Cl ratio, commonly used indicators of marine-origin air masses, were evaluated for all three sites. The analysis used intercomparable National Atmospheric Deposition Program (NADP)/Mercury Deposition Network (MDN) data for 2000-2002. Concentration and deposition data for wet-only precipitation were downloaded from the World Wide Web for MDN (Hg) and co-located major ion sites ME98 (Acadia National Park-McFarland Hill, Maine), WI36 (Trout Lake LTER, Wisconsin), and two sites in South Carolina which we treat as one unit: SC19 (Congaree Swamp, South Carolina), and SC06 (Santee National Wildlife Refuge, South Carolina).

Both NADP and MDN data were screened for validity using recommended NADP protocols (only samples with a validation code of 'w' or 'wa' were used in the analysis). The ions of interest were Cl and SO_4. One concentration of Cl was below detection limit in a WI36 sample, and assigned a concentration of half the detection limit. We evaluated 143 Hg observations for WI36, 110 for SC19, and 134 for ME98, collected between January 4, 2000 and December 31, 2002. For the same period, we evaluated 136 Cl and SO_4 observations for WI36, 102 for SC19, and 137 for ME98. Data were analyzed on a calendar year basis; therefore, winter periods represent January, February, and December in the same calendar year. We calculated the ratio of SO_4:Cl (division of the values, in mg/L), and calculated "precipitation-normalized concentration" of Hg as in Mason *et al.* (2000).

3. Results and Discussion

Based on the earlier PRIMENet research, we expected certain differences in biogeochemical processes between Cadillac (burned) and Hadlock (unburned) that reflected a depletion in ecosystem pools of constituents such as C, N, and Hg as a result of the original fire and the subsequent changes in vegetation composition. Cadillac generally had lower soil organic C, and along with that lower pools of most of nutrients and contaminants (e.g., Hg) that we measured. This was a result of losses due to combustion and volatilization during the 1947 fire, and an altered condition of biogeochemical cycling since the fire due to decreased total forest cover (reflecting erosion after the disturbance) and an increased dominance of hardwood species in the forest. Hadlock appeared to have a significantly higher ecosystem pool of C, nutrients and metals, but likely had a slower rate of cycling for them all. Added to the differences would be the potentially higher rates of atmospheric deposition under the coniferous canopy due to the greater efficiency of capture for this forest type.

3.1. Paired Watershed Stream Chemistry and Mass Balances

Discharge-weighted mean cation concentrations in streamwater were similar between watersheds (Table 3; Figure 9). ANC, pH, and Cl tended to be higher in Cadillac streamwater, while SO_4, NO_3, DOC and Hg were higher in Hadlock streamwater for all project years. In both watersheds, H^+, NH_4, NO_3, and Hg data suggest a net retention soils and vegetation; Na, Cl, Ca, Mg, K, and SO_4 indicate a net loss from the system for water years 2000 - 2003 (Nelson *et al.*, in press; Figure 11; Table 4), based on the flux components included in this analysis. Cadillac Brook watershed retains more Hg and NO_3 than Hadlock in every year of the study.

For some ions, differences related to vegetation and/or soils control the relative patterns of retention and release. For other ions, dry deposition is a major component of watershed inputs. For instance, Cl and SO_4 are typically considered conservative with respect to biota. Throughfall deposition of these solutes was 2-3 times (SO_4) and 2-10 times (Cl) wet deposition in these watersheds, dependent on season (Nelson, 2002). Throughfall deposition of these conservative ions at conifer sites – such as Hadlock Brook watershed – tends to be greater than at hardwood sites – such as Cadillac Brook watershed (Nelson, 2002). The increased scavenging efficiency at Hadlock Brook watershed helps to explain differences in the mass balances between watersheds when only wet precipitation is considered. Measurement of dry deposition is important for more accurate mass balances.

Ninety-five percent of the total Hg deposited on Cadillac watershed was retained by the watershed and eighty-seven percent of the total Hg deposited on Hadlock watershed was retained by the watershed, despite the higher export of Hg in streamwater from Hadlock (Table 4). Differences in the input of Hg *via* throughfall may equalize the Hg mass balance on the watershed scale (Johnson *et al.*, in press). Although 2004 fluxes, including the newly-collected throughfall data, are not yet finalized, streamwater chemistry indicates that the mass balances will continue to follow the same pattern of flux and retention, assuming the throughfall inputs are similar to those for 2000 calculated by Johnson *et al.* (in press). Thus the original PRIMENet hypothesis that the burned watershed would export less Hg than the unburned watershed continues to be supported. However, peak stream discharge increased every year since 2000, the

first full year after USGS gauges were installed, indicating the importance of inter-annual variability. Previous research in these watersheds (Johnson, 2002) and elsewhere (e.g., Shanley, 2004) have indicated that a few large hydrologic events may be responsible for most of the Hg exported in streamwater each year. Continued long-term monitoring, including hydrologic event sampling, and long-term data analyses are effective tools for evaluating these patterns.

Major forest fires are relatively infrequent in the Northeast; however, recent evidence suggests that when fires do occur, they have dramatic and lasting effects on N retention in forested watersheds (Figure 12). In a regional survey of 159 small, forested watersheds in central New England, the Cone Pond Watershed in New Hampshire was one of only three watersheds having no detectable NO_3^- in streamwater (Hornbeck *et al.* 1997). Soil denitrification rates at Cone Pond are low, giving rise to the hypothesis that a severe fire in 1820 disrupted N dynamics to the extent that present conditions are still unfavorable for nitrification (Hornbeck and Lawrence 1997; Campbell *et al.*, 2004). The Cone Pond findings suggest that fire and accompanying volatilization of a large pool of N nearly two centuries ago are cause for the Cone Pond watershed being unable to generate NO_3^- beyond that immobilized by microbial and plant uptake. Preliminary sampling at the outlet of an unburned sub-catchment near the top of Cadillac Brook watershed showed NO_3^- concentrations in streamwater similar to those at undisturbed Hadlock Brook, supporting the hypothesis that fire history plays an important role in N retention and flux at these watersheds.

The results of the long-term monitoring funded by both EPA-PRIMENet and this funding, suggest that N is strongly retained in burned watersheds. These data have led to yet more questions: how does fire instensity affect N retention? If there are critical thresholds above which N will begin to 'leak' from previously burned watersheds? The implications of this research are relevant for the Clean Air Act and changes in landcover/land use. Since implementation of the Clean Air Act, N deposition at Acadia has remained fairly constant (~10 kg NO_3/ha/yr; ~3.5 kg inorganic N/ha/yr; NADP data, 1984-2005). How long will it take at current deposition levels to saturate Cadillac Brook watershed? Also, is there a difference between forests burned in fires and those re-set to earlier successional trajectories by other disturbances, including land-use change? We are currently seeking funding to evaluate these patterns using a chronosequence of burned watersheds in the Northeast, anchored by Acadia and Cone Pond.

3.2. Throughfall

3.2.1. Background Information from PRIMENet-funded Research

Earlier research funded by the PRIMENet program measured atmospheric deposition of Hg and major ions to 78 sites in the paired watersheds, Cadillac and Hadlock (Kahl *et al.*, 1998; Nelson, 2002; Johnson, 2002). Weathers *et al.* (1998) used resin-type collectors to measure S deposition at 300 sites across Acadia. The purpose of the PRIMENet throughfall research was to determine which (if any) landscape factors were driving spatial variability in deposition to Acadia. It is well documented that atmospheric deposition of pollutants to complex terrain is not spatially uniform (Cronan and Reiners, 1983; Lovett *et al.*, 1999; Weathers *et al.*, 1992, 1995, 2000). This heterogeneity is especially significant at Acadia National Park because of the steep, varied

topography and the differences among vegetation types in terms of age and stand composition (Weathers *et al.*, 2001).

Using the 2000-2001 throughfall data from Cadillac and Hadlock watersheds, vegetation type was found to be the most important factor driving deposition in each watershed for each season. Throughfall flux of indicator ions Cl^-, SO_4^{2-}, and Na^+ at deciduous sites was generally lower than at coniferous and mixed sites, although not always significantly different. Scrub/open and mixed sites were significantly different than coniferous (ANCOVA, $P<0.02$), with scrub/open throughfall flux lower than all other vegetation types. At both watersheds, enhancement followed the general pattern: coniferous ≈ mixed > deciduous > scrub/open for these indicator ions (Table 7). In a throughfall study in New York, enhancement factors (EFs) calculated using forest floor lead (Pb) as an index for deposition were 2.5 for conifer sites and 1.0 for deciduous sites on west aspects (Weathers *et al.*, 2000), consistent with these results; for conifers, SO_4^{2-} enhancement was ~2.5, and for deciduous sites enhancement was ~1.5 (Table 8).

Both landscape aspect and vegetation type were the most influential factors affecting Hg deposition in 1999-2000 in Cadillac and Hadlock watersheds (Johnson, 2002). Sites that face south to southwest received the highest Hg deposition, presumably due to the interception of continental contaminated air masses and prevailing wind direction. Deposition of Hg at mixed forest sites was consistently higher than at either coniferous or deciduous sites (Figure 13). Presumably the multi-layered canopy architecture creates the maximum air mass contaminant interception capacity, similar to the edge effect reported by Beier *et al.* (1992) and Weathers *et al.* (1992; 1995; 2000), and the aerodynamic roughness effect reported in Rustad *et al.* (1994). In Cadillac Brook watershed, the mixed type consists of early successional deciduous vegetation (35 to 50 years old) with a regenerating spruce-fir understory, interspersed with a few large conifers and maples that survived the fire. The few mixed sites at Hadlock were primarily spruce and birch, and often appeared to be breaking up. This research highlights a need to understand and measure the range in canopy architecture in the context of atmospheric deposition to forested sites. Methyl Hg (MeHg) deposition was not affected by these factors.

In the Weathers et al. sites (300 park-wide), elevation and vegetation type were identified as key factors influencing deposition of S across the park. Use of those results to develop a hotspot map for S deposition at Acadia was reported in Weathers et al. (2006).

Qualitatively, enhancement at shrub/scrub sites was lowest at Cadillac Brook watershed and enhancement at open sites was lowest at Hadlock Brook watershed (Table 7). At Cadillac Brook watershed, summit shrub communities tended towards deciduous species, while at Hadlock Brook watershed, coniferous vegetation dominated summit shrublands. Future research could focus on these less-frequently studied areas to better quantify the effect of scrub/shrub species composition on deposition.

Differences in watershed and vegetation characteristics control the input of water and major ions to these watersheds because vegetation type influences throughfall chemical and hydrologic inputs (e.g., Houle *et al.*, 1999; Lovett *et al.*, 1996; Cronan and Reiners, 1983). At Hadlock Brook watershed, the greater scavenging efficiency and year-round foliage resulted in greater SO_4^{2-}, Cl^-, and Na^+ concentrations and lower pH in throughfall than in Cadillac Brook watershed

(Nelson, 2002). Throughfall SO_4^{2-} was two- to three-times wet deposition, in the range reported for SO_4^{2-} for the Bear Brook Watershed in Maine (Rustad *et al.*, 1994).

Precipitation and throughfall volume and chemistry measurements (Tables 5a, 5b, and 6) were coupled to hydrologic flux via stream waters by determining watershed mass balances (Johnson, 2002; Nelson, 2002). Seasonal differences were important, with highest dry deposition of major ions (inferred from throughfall:wet deposition) in fall and summer. However, National Atmospheric Deposition Program data indicated that wet deposition inputs of Cl and Na were highest in winter, influenced by sea spray and marine storm tracks. It is likely that there is a complex suite of processes influencing throughfall composition, such as higher particulate deposition during the dry summer months from wind-blown aerosols, and higher marine deposition in winter based on prevailing wind patterns and storm tracks. Ongoing research is quantifying winter deposition in these study watersheds.

3.2.2. New Data from this Project

In 2004, we collected throughfall seven times at each of 21 throughfall collection sites. Data from 2004 were consistent with those collected in the earlier research (Nelson, 2002; Johnson, 2002)(Table 6). As in the earlier studies, concentrations of major ions (except NO_3), DOC, and Hg in throughfall solutions were highest at Hadlock Brook watershed and lowest at the bulk site at McFarland Hill (Table 6). Notably, the 2004 throughfall database included both Hg and major ion chemistry at every site sampled, while in previous research, Hg was not sampled at every site due to logistics and costs. For this project, Hg was sampled in sites with shrub/scrub vegetation, a landscape type not included in the earlier research. These throughfall data were used to evaluate spatial patterns and develop a model for deposition of S and Hg.

3.2.2.1. *Chemical relationships and spatial patterns.* Based on the literature and our earlier data set, we had several hypotheses regarding relationships among throughfall chemical variables and landscape variables. We expected:

1. Negative correlation between concentration of most analytes and water volume (Weathers, pers. comm.);
2. Positive, significant correlation between Hg and SO_4;
3. Vegetation type and deposition would be statistically correlated, and;
4. Canopy openness would be more important than previously thought. Although there were no significant correlations with canopy cover as measured by Li-Cor in the 1999-2001 data, our new method of canopy photography to measure canopy openness produced a notably different set of measurements with a broader range and more logical distribution (Figure 10), and we evaluated the new canopy openness data in addition to the previously established database of landscape attributes.

Results from the watersheds at Acadia were consistent with those from published throughfall research (Table 9). Throughfall chemistry varied by forest type due in part to ion exchange reactions that occur more readily in deciduous canopies (Cronan and Reiners, 1983; Matzner and Meiwes, 1994; Bailey *et al.*, 1996; Lovett *et al.*, 1999; Houle *et al.*, 1999b; Weathers *et al.*, 2000). Deciduous throughfall generally had a higher pH due to ion exchange of H for base

cations or a 'weak base buffering' effect, whereby the canopy released organic or bicarbonate salts (Cronan and Reiners, 1983). Throughfall under coniferous, as opposed to deciduous sites, typically demonstrated a net acidification, likely due to NH_4 uptake or nitrification, washout of dry deposition, or leaching of organic acids from the canopy (Cronan and Reiners, 1983). Seasonally, greater than 70% of K in throughfall can be derived from foliar leaching (Houle *et al.*, 1999b). Deposition of Hg, Ca, Mg, Na, Cl, and SO_4 was highest at coniferous and mixed sites (e.g., Figure 13). Deposition of K was highest at mixed and deciduous sites. Open and scrub sites had the highest H (lowest pH), followed by coniferous sites. A reduction in NO_3 under the deciduous canopy suggests uptake in both watersheds, regardless of stand age.

We evaluated bivariate scatterplots for all throughfall and landscape variables, and calculated a correlation matrix between all variables, reported here as Pearson's Correlation Coefficient (r), which determines a linear correlation between two variables. Volume of water collected in the Hg sampler was strongly correlated (r=0.98) to water volume in the major ion sampler. This result suggests that the two sides of the collector could be treated as a single sample from a site, though the collector had to be split for logistical reasons. As expected, there was a weak negative correlation between water volume and concentration of major ions and Hg. There were significant (defined here as r>0.5) correlations between specific conductance and all major ions except NO_3, and between specific conductance and DOC. DOC was correlated with all major ions except NO_3. Hg was not correlated with any other solute, but was weakly correlated with summer canopy openness (r=0.46). No other chemical parameters correlated significantly with any landscape features, suggesting that non-linear statistical approaches were necessary to determine patterns that could be used for modeling.

Using the newly-collected 2004 throughfall data, we repeated the ANCOVA (analysis of covariance) analysis of Nelson (2002), including Hg throughfall data. The ANCOVA, run using SYSTAT software, uses both categorical and continuous data to develop relationships between variables using both regression and ANOVA approaches in combination. We evaluated ANCOVA results for Hg (n=124), SO_4 (n=140), Cl (n=140), Ca (n=140), NO_3 (n=140), and specific conductance (n=139). Both specific conductance and Ca were good indicators of all cations, with strong correlations. Canopy openness was the best predictor for Hg ($P<0.001$)(Figure 14), SO_4 ($P<0.05$), and Ca ($P<0.004$). Vegetation type was the best predictor for Cl ($P<0.05$) and specific conductance ($P<0.08$)(Figure 15), a logical result since throughfall solutions were largely dominated by salt inputs, and vegetation type was also important for Hg ($P=0.001$). Other significant landscape effects were elevation for Ca ($P=0.09$) and Hg ($P=0.014$), burn status for Ca ($P=0.004$) and Hg ($P=0.05$), and aspect for Ca ($P=0.012$).

Unlike the 2000 data analysis (Johnson, 2002), aspect was not important for Hg deposition, perhaps due to the smaller sample size. Because both watersheds face generally southward, this experimental design was not conducive to determination of the effects of aspect. No landscape factors were important in explaining variability in NO_3 concentrations for these sites. Although vegetation type continued to be important as in the earlier data analyses (Nelson, 2002; Johnson, 2002), canopy openness superseded vegetation type as the most important factor driving deposition of Hg, SO_4, and Ca.

Increased deposition often occurs at higher elevations due in part to orographic rain enhancement, frequent fogs and higher windspeeds at elevation (Lovett *et al.*, 1999; Weathers *et al.*, 2000). The decrease in canopy coverage at elevation may also offset the elevation effect at Acadia. Most areas above 300 meters are sparsely vegetated in both watersheds, reducing canopy interception of fogwater and dry deposition, thus de-emphasizing the typical enhancement effect of elevation on deposition.

The new throughfall data reinforced earlier findings which suggested that vegetation type and elevation are important drivers for deposition of major ions, including SO_4, Ca, and Cl, and Hg. Strong correlations in this new data set between specific conductance and major ions plus DOC indicate that some of the landscape controls may affect almost all chemical constituents, supporting the idea that a deposition model for one analyte may be transferred to other analytes in many cases. The exception was N; there were no significant correlations or ANCOVA results for NO_3 or NH_4 with any other measured variable. Because it is taken up by vegetation, N deposition at forested sites was not significantly different than that collected in the open. Throughfall is not an appropriate methodology to quantify total N deposition. The work of Weathers *et al.* will continue to evaluate the possibility of using S as a surrogate for N deposition. For Hg, the strongest correlation and most predictive landscape feature was canopy openness, a variable newly determined for this project that is proving to be important (Figure 16). We suggest that canopy openness takes into account both vegetation type and canopy architecture, and providing a measure of both that changes with the seasons, unlike the static vegetation type variable. Canopy openness was measured in both summer and winter at Acadia, and ongoing research is evaluating whether it can also be used to model winter deposition (Nelson, in progress).

3.2.2.2. *Seasonal patterns.* Atmospheric deposition varies not only spatially, but also seasonally, both in response to weather patterns and changes in forest canopy architecture due to leaf drop. We investigated the only data source for year-around deposition data, the NADP/MDN, to determine the seasonal pattern in wet deposition at Acadia. We proposed that the seasonal patterns evident in NADP/MDN data may be used as a baseline for modeling deposition in other seasons. Although air masses generally track from west to east in summer, many winter storms track northeast along the Atlantic coast in winter. Monitoring at Acadia shows that significantly more seasalt is deposited in winter (National Atmospheric Deposition Program, 2003), possibly due to this seasonal shift in general weather patterns and storm type. In Maryland, winter (December to February) deposition of Hg was only 10-20% of annual flux to four sites, and winter deposition of Hg was even less (~5%) in Wisconsin (Mason *et al.*, 2000). Mason *et al.* (2000) attributed this low winter deposition to 1) less efficient scavenging of particles by snow and 2) inhibition of in-cloud oxidation of Hg^0 by cold temperatures. Because of Acadia's island situation and site-specific weather patterns, we hypothesized that Acadia receives significant marine-derived Hg, and precipitation water flux ultimately drives seasonal patterns in Hg deposition.

We compared the Acadia NADP/MDN site ME98 to sites in WI and SC, sites chosen to repeat the Mason *et al.* study (2000), to determine whether winter deposition is important in this geographic area. For all three sites in all three study years, the median precipitation-weighted Hg concentration was highest in summer (June-August) (Figure17g.-i.). Hg concentration was

lowest in winter (December-February) for all sites and years except 2000 at ME98, where fall (September-November) concentration was slightly lower than winter concentration. The range of Hg concentration values was greatest for ME98, followed by SC19, and finally WI36 (Table 10). Mean concentration was highest for SC19, followed by ME98, then WI36.

Deposition of Hg was highest in spring (March-May) for ME98 for all years, highest in summer for WI36 for all years, and highest in fall for SC19 for 2000 and 2001, with spring deposition slightly higher than fall in 2002 for SC19 (Figure 17a.-c.). For both WI36 and SC19, winter deposition was lower than for all other seasons for all years. For ME98, winter deposition matched or exceeded fall deposition in all three years, and also exceeded spring deposition in 2001.

The pattern of precipitation resembled deposition for the three sites (Figure 17d.-f.). Precipitation was greatest in summer for WI36, in fall for SC19 (except 2001 when spring precipitation slightly exceeded fall), greatest for spring for ME98 in 2000 and 2002, and greatest in winter at ME98 in 2001. Precipitation data were available from the National Oceanic and Atmospheric Administration (NOAA) National Climatic Data Center, available online at http://cdo.ncdc.noaa.gov/ancsum/ACS. Average annual precipitation for 2000-2002 was: 117 cm for Acadia National Park, Maine; 96 cm for Sumter, South Carolina; and 89 cm for Minoqua Dam, Wisconsin. Average annual snowfall for 2000-2002 was: 195 cm for Acadia National Park, Maine; 3 cm for Sumter, South Carolina; and 328 cm for Minoqua Dam, Wisconsin. Annual and seasonal fluxes of Hg were calculated for each site, with the percent of annual flux for each season at each site (Table 11). For sites WI36 and SC19, winter deposition was consistently the lowest proportion of annual flux, ranging from 2.8% to 7.1% at WI36 and 8.2% to 14.9% for SC19. For site ME98, winter flux accounted for 16.6% to 27.5% of annual Hg flux via wet deposition.

Concentrations of Hg and Cl were plotted for the three study sites to evaluate their relative seasonal patterns. Concentration of Cl at site WI36 was generally well below 5 μeq/L and did not exhibit strong seasonal patterns. The concentration of Hg at WI36 showed the higher relative concentration in summer in the three study years (Figure 18a.).

For SC06, concentration of Cl was generally below 40 μeq/L, with the notable exception of a single measurement of ~600 μeq/L on November 20, 2001, that was most likely due to the low sample volume (only about 0.5 mm of precipitation) and the drought that preceded this rain event, with no valid samples for at least a month prior to this collection (Figure 18b.). In general, Cl concentration for this site was rather noisy and appeared to reflect discrete events rather than seasonal patterns. Slightly higher Hg concentration in summer of each year was observed for SC19.

At site ME98, Cl concentration was generally below 20 μeq/L during summer and below 60 μeq/L in winter, with spikes from 80 to 180 μeq/L in winter (Figure 18c.). The ME98 site did exhibit a seasonal increase in mean Cl concentration in winter. Hg concentration at ME98 was out of phase with Cl concentration, with slightly elevated values in summer and relatively low values in winter. Hg concentration was typically below 20 ng/L with discrete summer events having concentrations up to 80-100 ng/L.

The results from this data analysis corroborate those from Mason *et al.* (2000) for the mid-Atlantic and Wisconsin regions, with 10-15% of annual flux in winter for Maryland and South Carolina and <5% for Wisconsin and Minnesota. Mason *et al.* (2000) did not evaluate New England sites at that time, and our research indicates a different seasonal distribution of Hg deposition for site ME98.

Despite the higher Hg concentration in summer at all three sites, the Maine site had a high percent of its annual flux in winter as compared to the other two sites. It is not likely that the temperature effect discussed by Mason *et al.* (2000) is the cause of higher deposition for Maine, because Maine temperatures are cooler than those in Maryland and cooler temperatures should produce less Hg deposition if cloud-based oxidation is an important mechanism.

Mason *et al.* (2000) also implicated less efficient scavenging of Hg by snow as a possible explanation for less Hg deposition in winter. The results of this study do not support that hypothesis that Acadia National Park receives more of its annual precipitation as snow than coastal Maryland, the site of the Mason study. If snow scavenging efficiency were less than rain, and if the amount of precipitation received in winter were the same (whether snow or rain), we would expect less winter deposition at the Acadia site than at the Maryland site.

Precipitation amount may partially explain the larger winter deposition for ME98. The annual precipitation for WI36 ranged from 0.8 to 0.9 m, for SC19 from 0.9-1.0 m, and for ME98 from 1.2 to 1.6 m, except during the extreme drought year 2001, during which precipitation at ME98 was about 0.6 m. The difference between sites, about 0.3-0.5 m, appears to be accounted for by much greater winter and spring hydrologic flux in Maine and slightly lower hydrologic flux in summer in Maine. Maine has fewer convective storms than other parts of the continental U.S. east of the Rocky Mountains, partially explaining less precipitation in summer (Zielinski, pers. comm.).

A goal of this portion of the study was to determine whether marine-derived Hg could be an important source of Hg during winter and early spring at Acadia National Park as compared to other sites. Comparison of Cl and Hg concentrations at Acadia for three study years showed that Hg and Cl were out of phase: Hg concentration was highest in summer and Cl concentration was highest in winter. Winter Hg deposition for Acadia could represent as much as 27.5% of annual flux, and winter and spring Hg flux combined was 65% and 57% of annual flux for the non-drought years. Winter precipitation water inputs were far greater in Maine than at the other sites in winter, partly explaining higher Hg deposition.

To assess the possible contribution of marine air masses to Hg flux, the SO_4:Cl ratio was calculated for each of the three sites, for each observation. The approximate value of SO_4:Cl (concentration in mg/L divided by mg/L) in ocean water is 0.14 (Stumm and Morgan, 1996). Therefore, ratios near 0.14 are interpreted as derived from marine sources, and much higher ratios likely represent less marine influence or excess SO_4. Similarly, we plotted Na versus Cl for throughfall collected during this project, and for snow throughfall collected as part of ongoing research (Nelson, in progress). If the ratio Na:Cl is approximately 0.86, the source of a water sample can be attributed to marine inputs, because Na:Cl in seawater is 0.86. For snow, Na:Cl

was 0.95, slightly higher than in seawater, but values were remarkably similar for every sample point (Figure 20). For rain throughfall, Na:Cl averaged 0.88, very similar to that in seawater. However, there was more variability in the rain Na:Cl values than snow, indicating that specific events or air mass trajectories may play more of a role in determining deposition in summer than in winter.

The SO_4:Cl ratios were plotted for the three sites (Figure 19). We expected very little marine influence at site WI36 due to its inland location, and some marine influence at SC06 and SC19 because of proximity to the ocean. We expected distinct and frequent marine influence for the Acadia National Park site ME98 because the Park is located on an island, and is often affected by storms that track along the coast. Though qualitative, the plots of SO_4:Cl support these expectations. For WI36, the ratio was typically between 10-30 with higher ratios in summer, indicating increased SO_4 concentration in summer (Figure 19a.). For SC06, the ratio was usually 1-20 with some higher values in summer, but with no clear pattern (Figure 19b.). For ME98, the ratio was typically well below 5 for October through April, and values from 1 to 20 or higher in summer (Figure 19c.). Frequent ratio values quite close to zero – marine SO_4:Cl is 0.14 - indicate strong seasonality, and that the Acadia site was indeed affected by marine air masses in the winter in these three study years.

Seasonal Hg concentration patterns agreed between three sites in different regions: concentration was highest in summer of the three study years. However, seasonal patterns in Hg deposition were different between the three sites. The least winter deposition occurred in Wisconsin, and the most occurred for a coastal Maine site. Mason *et al.* (2000) explained lower winter deposition in Maryland as compared to the rest of the year by 1) less efficient scavenging by snow and 2) cloud processes that would be inhibited by colder temperatures in winter. These hypotheses do not fully explain the higher deposition in Maine in winter.

Using seasonal patterns of Cl and the ratio of SO_4:Cl in wet deposition, this portion of the study has shown that air masses track over ocean water in winter at Acadia National Park. More study is required to determine whether - and how - marine storms contribute marine-derived Hg to ecosystems at Acadia. The global Hg budget determined by Mason *et al.* (1994) estimated oceanic evasion of Hg as 10 Mmol/yr, and the contribution of anthropogenic Hg from fossil fuel burning as 20 Mmol/yr. Much of the Hg evaded for the ocean is in rapid equilibrium with the atmosphere and is ultimately from historic anthropogenic deposition to oceans (Mason *et al.*, 1994). The study was unable to quantify the magnitude of such marine-derived deposition of Hg, a potential focus for future research. The study also determined that precipitation amounts differed significantly among the three sites, and increased hydrologic input to Acadia in winter is likely to be a major driver of the relatively high winter deposition.

3.3. Modeling Deposition

Based on the landscape relationships with throughfall deposition, and the evidence suggesting that multi-variate models may explain the observed patterns (Figure 16), we developed regression tree models for SO_4 and Hg deposition. We evaluated several regression trees using the 2000 data that coincided with the sampling period of Weathers *et al.* The suite of potential predictor variables entered into the modeling procedure were: elevation, vegetation type, canopy

openness, aspect, burned/unburned status, watershed, USGS Vegetation Map veg code, USGS Vegetation Map height, USGS Vegetation Map distribution. In all resulting models, the most important splitters were canopy openness or vegetation type (either map- or site-derived), elevation, and aspect. The importance of canopy openness has not been discussed in the literature, and merits further investigation. Also, canopy openness is not a useful predictor variable for island-wide prediction, since it was only measured in the paired watersheds. However, simple regression analyses showed that canopy height categories, available for the entire park in the USGS-NPS vegetation map attribute table (Lubisnki *et al.*, 2003), could be used as a proxy for canopy openness based on the small watershed data (R^2=0.57). Rudnicki *et al.* (2004) report a similar relationship between height and cover in lodgepole pine, although the relationship may break down for much older canopies with crown competition or abrasion (A.S. White, pers. comm.).

Most modelers strive toward parsimony, or finding the simplest model that provides the best and most realistic range of predictions. The key tradeoff is that making the model simpler – usually by using fewer predictor variables – can lead to predictions that do not describe the system very well. In this throughfall research, the range of actual values of S deposition in 2000 was 0.3 – 28 kg/ha/yr, with a mean value of 7.97 kg/ha/yr. The range of predictions from the tree developed from all predictors in 2000 was 3.7-20 kg/ha/yr of S, narrower than the range in the actual measured data. Thus, if we were to use this model to predict throughfall, we would expect that hotspots and coldspots would be dampened, and the model would predict less variability than we would probably see if we measured throughfall. Pruning, or simplifying, trees resulted in a further compressed range of deposition predictions, with minimum values close to the average measured deposition value. The simpler the model, the more the extremely low and extremely high predicted deposition values were lost. Thus, the model moves toward becoming an average rather than describing site-specific variability. The data and results confirm that predicting throughfall deposition is complex. Proportional reduction in error, similar to an R^2 value, was 0.24 for the tree described above, indicating that the model needs some refinement before it may be useful. However, tree structures made logical sense and were corroborated by univariate relationships with landscape factors reported in the literature.

Regression tree model results are being compared to results from the Weathers *et al.* (in revision) empirical model developed for the entire park. Ongoing discussions and manuscript preparation include spatial merging of results and data, and use of the 2004 throughfall data as a validation set. Regression tree analyses supported including vegetation structure in deposition models, and indicated that canopy height may be used as a surrogate for canopy coverage if further site-specific validation is conducted. The CART model corroborated the basic premises of the Weathers model: vegetation characteristics and elevation were indeed the most important landscape factors affecting throughfall variability at Acadia.

3.4. Summary of Deposition Patterns and Modeling

Throughfall data from 2004 suggested that we can represent the landscape with fewer field sites. As described in the methods, we used cluster analysis to select a representative site from each major landscape-chemical condition, resulting in 21 sites as compared to the 78 sampled in 1999-2001. For Hg, the range in rain throughfall concentration for 2004 was 2.06-36.6 ng/L,

with a mean of 12.8 ng/L. Johnson (2002) reported Hg concentrations from 2.1-68.4 ng/L; only 5% of the 555 observations in 1999-2000 were greater than the maximum of 36.6 ng/L reported for the 2004 data set. For specific conductance, 15% of samples in 1999-2001 were greater than the maximum for 2004, but over 2/3 of these high-concentration samples were taken during Hurricane Floyd in 1999, immediately following drought in 1999, or during 2 extreme rain events in November of 1999. Entire sample sets for each of these dates were greater than the 2004 maximum, presumably attributed to these extreme weather events. We conclude that this smaller set of sites is representative of the range of chemical concentration, and would be adequate for long-term monitoring of throughfall, or periodic re-validation of model results.

This project laid the groundwork creating more accurate, spatially explicit deposition estimates for several ions across Acadia National Park. We calculated new landscape metrics, and determined which landscape factors control variability in deposition across the two small watersheds. While vegetation type was still an important determinant for deposition of most major ions and Hg, the newly-measured canopy openness variable was equally or more important for Hg and SO_4. Although canopy openness requires measurement at each individual site, early results suggest that canopy height, available for the entire park as an attribute of the USGS-NPS vegetation mapping project GIS coverage, could be a reasonable surrogate for canopy openness.

We modeled deposition for SO_4 and Hg across the entire park, using relationships from the small watersheds and a multivariate regression tree model that depended heavily on canopy openness and elevation (Figure 21). These factors are similar to those that underpin the deposition model of Weathers *et al.* (2006) for the entire park. By comparing the two spatial scales – small watersheds (this study) and park-wide (Weathers *et al.*) we will be able to better elucidate confounding factors, such as changes in vegetation structure at summits, and incorporate this new understanding into the ongoing collaborative work. Further comparison will also yield information regarding uncertainty and variability in model predictions.

Finally, we have evaluated seasonal patterns in wet deposition and begun to evaluate seasonal throughfall patterns as part of both this project and ongoing research (Nelson, in progress). Hg and SO_4 wet deposition are greatest in summer and least in winter, while Cl deposition is greatest in winter and least in summer. Initial results from snow throughfall collection in winter 2004/5, immediately following the throughfall season for this research, indicate that throughfall deposition of seasalt aerosols is also greater in winter than summer. This seasonal pattern provides a starting point by which to model deposition year round at Acadia.

3.5. Comparing Modeled Deposition to Streamwater Chemistry

We sampled 28 stream sites in Acadia National Park for the one-day stream survey. Although we collected soon after a fall rain event, flows in some streams were still relatively low or too low to sample, particularly at upland sites like the Cadillac Mountain Summit. Some streams were sampled by Kahl *et al.* in 1984 and others by Peckenham *et al.* in 1999 and 2000. The sites sampled for this project were determined using cluster analysis based on all previous research, and identified stream sites with the widest range of chemical conditions and landscape positions for the survey. For this project, streamwater equilibrated pH values were between 6.4 and 7.6,

except for Hodgdon Brook and Steward Brook, both ~4.7. DOC ranged from 0.9 to 23 mg/L, with an average of 6.1 mg/L. Total Hg concentration ranged from below the analytical detection limit (0.4 ng/L) to 6.49 in Squid Cove Brook (Figure 22). Oak Hill Stream also had high Hg, 6.26 ng/L, and high DOC, 25 mg/L. In previous work, the highest Hg value was 5.07 at Oak Hill Stream (Peckenham *et al.*, in press). Oak Hill Stream and Squid Cove Brook are located in the northwest quadrant of Mount Desert Island (Figure 22). Oak Hill Stream drains a large wetland area and was sampled at the wetland outlet. Squid Cove Brook drains a small wetland farther upstream from the sample site, but appears to meander through lowlands and between hills before reaching the sample site. The Oak Hill Stream Hg value corroborates that from the earlier surveys (Peckenham *et al.*, in press), but Squid Cove Brook Hg was considerably higher than in the earlier survey and should be re-sampled before conclusions can be drawn.

We mapped the modeled SO_4 and Hg deposition across the park, based on the CART analyses. For SO_4, the model depends on canopy openness, elevation, and aspect. For Hg, the model depends only on canopy openness. The model shows highest SO_4 deposition on a few mountaintops, and moderate deposition across the park, especially on the western and southern portions of Mount Desert Island, roughly the un-burned area (Figure 21). Eastern MDI and rocky, bald summit mountains have low modeled deposition. For Hg, only two deposition estimates resulted because of the simplistic nature of the model: high versus low Hg deposition. High deposition areas are roughly the same as for SO_4 (Figure 21).

Overall, streamwater SO_4 concentrations followed a similar pattern, with the highest values in western and southern sections, especially clustering around Hadlock Pond and watershed and the western mountains (Figure 21). Lower SO_4 values were located in the burned zone, and northwest quadrant of the island. Streamwater Hg values did not follow the same pattern, with the highest values in the northwest quadrant (Figures 21, 22). With exceptions, the lowest streamwater concentrations for both SO_4 and Hg were in the burned area of the park, near Cadillac Brook watershed and the Kebo Brook areas.

Although deposition of Hg and S appears to be driven by similar landscape factors (elevation, vegetation type and structure), further research will be necessary to determine what factors drive Hg in streams across the park. Our stream survey was a one-time snapshot of Hg concentration. However, many of the highest Hg values in streams were in areas known to be influenced by wetlands. The limited data suggest that future research should evaluate the role of wetlands in mediating Hg transport from deposition to streams.

3.6. Acadia Streams Database

Including the results of the stream survey collected as part of this project but excluding the thousands of observations from the paired watershed study, we assembled a database of over 1200 observations for streamwater chemistry at Acadia National Park, spanning a time period from 1982-2004 (Figure 6). Most of the samples in the database include full ion chemistry, and 161 include data for Hg. The database includes the first island-wide survey of streams (Kahl *et al.*, 1985), the first intensive watershed study at Hadlock Brook (Heath *et al.*, 1992), and other projects which have sampled some of the same sites, and some new sites.

A draft database has been transferred to the National Park Service at Acadia (B. Gawley), and the final database with metadata is included as a digital appendix with this report (Appendix G). In addition, the data have been transferred to Peter Vaux of the UMaine Mitchell Center, for posting on PEARL, Maine's Environmental Information web site (pearl.maine.edu), and SPARC, a web site under development that lists information on studies in calibrated watersheds in National Parks (www.umaine.edu/sparc). These web-accessible data repositories allow access to the data by researchers, agency staff, the public, and students and educators. The data can be used to select sites for future studies, to characterize water quality across the park, or to access historical records for time series analyses. For this research project, we used the database to select sites for the stream survey. A GIS layer including all of the sites, indexed by project name, is also included in the digital appendices to this report (Appendix F).

3.7. Litterfall Deposition

Hg deposition to the landscape is typically evaluated using data from precipitation Hg deposition. Litterfall is also an important flux for Hg to soils in forested landscapes, yet much less is known about litterfall Hg. We measured litterfall Hg contributions to Hg deposition in Hadlock Brook and Cadillac Brook watersheds. Litterfall was collected at 39 sampling sites in 2003 and 2004 and analyzed for total Hg (Figure 7). Four vegetation classes were designated in this study: hardwoods, softwoods, mixed and scrub. Complete results from this litterfall research can be found in Sheehan (2005) and Sheehan *et al.* (2005), as well as Appendix H.

The estimated annual *deposition* of Hg via litterfall in Hadlock Brook watershed (10.1 $\mu g/m^2$) and Cadillac Brook watershed (10.0 $\mu g/m^2$) was greater than precipitation Hg deposition and similar to or greater than the magnitude of Hg deposition *via* throughfall (Figure 23). These results demonstrate that litterfall Hg flux to forested landscapes is at least as important as precipitation Hg inputs.

The mean litter Hg *concentration* in softwoods (58.8 ± 3.3 ng Hg g^{-1}) was significantly greater than in mixed (41.7 ± 2.8 ng Hg g^{-1}) and scrub (40.6 ± 2.7 ng Hg g^{-1}), and significantly lower than in hardwoods (31.6 ± 2.6 ng Hg g^{-1}). In contrast, the mean weighted litter Hg *flux* was not significantly different among vegetation classes, because less mass of litter counteracted higher Hg concentration in litter at softwood sites. As with throughfall, landscape characteristics (i.e., aspect, elevation and canopy density) were significantly correlated with litter Hg concentrations and flux.

In a pilot study as part of this litterfall research, a significant negative correlation was defined between litter C:N and litter Hg concentrations. In decomposing litter, Hg was strongly bound to the non-labile components of organic matter. While the relationship between litter C:N and litter Hg does not indicate a cause and effect relationship, these pilot data suggest that bulk litter C:N is a potentially useful predictor of Hg concentrations. At a minimum, C:N may be an important litter quality variable to consider when evaluating litter Hg dynamics.

Synthesis of Landscape Characteristics and Litterfall Mercury. We found aspect, elevation and canopy density to often be significantly correlated with litter Hg concentrations and flux although most correlations were relatively weak. The confounding effects of simultaneous

differences in landscape characteristics and vegetation types obscured our ability to draw conclusions about direct linkages from this study. What does emerge from these analyses, however, is the predominant effect of vegetation characteristics on Hg dynamics in these extensively managed landscapes.

The proximity of ANP to the coast, and the fact that winds often originate from the open ocean to the south rather than west, likely also plays an important role in litter Hg deposition at this site. Since the flux of Hg emitted from oceans is estimated to be half as much as anthropogenic emissions and two times the flux of Hg emitted from natural terrestrial sources (Schroeder and Munthe, 1998), the assumption that Hg pollutant inputs are dominated by the westerly winds could be erroneous. Also, since this study site has the greatest relief along the entire east coast, it is impacted by coastal fog and clouds. Cloud water Hg concentrations are often much higher than the concentration of Hg in precipitation (Malcolm *et al.*, 2003; Miller *et al.*, 2005). Although no known research has been conducted on the Hg concentration of coastal fog, which frequently shrouds the ANP landscape, Weathers *et al.* (1986) and Jagels *et al.* (1989) documented very acidic fog at ANP (3.3 pH), indicating the pervasiveness of some atmospheric pollutants. Research on Hg in coastal fog, and documentation of its frequency and spatial distribution, would provide useful insights to understand Hg cycling at ANP.

Deposition of Hg in litter at ANP likely reflects a combination of climatic influences, proximity to the ocean, topography, and vegetation. Evers (2005) indicated that mid-coast Maine is a biological hot-spot for Hg accumulation, attributed in part to a combination of landscape characteristics. Further study is required to understand the mechanisms of influence of these landscape characteristics.

4. Summary of Key Findings

Objective 1. Continue the PRIMENet intensive watershed monitoring for stream chemistry and flow to enable calculation of elemental mass balances.

Key findings. This research provided a continuous (1999-2005) record of streamwater chemistry (e.g., Figure 24) and fluxes for paired watersheds at Acadia National Park, making the site one of the most intensively studied sites for Hg in the U.S. (Kahl *et al*., in press). Discharge-weighted mean cation concentrations in streamwater were similar between watersheds (Table 3; Figure 9). ANC, pH, and Cl tended to be higher in Cadillac streamwater, while SO_4, NO_3, DOC and Hg were higher in Hadlock streamwater for all project years. Cadillac Brook watershed retained more Hg and NO_3 than Hadlock in every year of the study. Thus the original PRIMENet hypothesis that the burned watershed would export less Hg and NO_3 than the unburned watershed continues to be supported.

Management implications. These long-term, high quality data sets provide context for newly-initiated Vital Signs monitoring implemented by NPS. At Acadia, the two paired watershed sites are sampled as intensive sites as part of Vital Signs. With continued long-term monitoring, NPS staff can evaluate trends in acidification and conductivity of these upland streams. In addition, the results point to the important role of site disturbance history in streamwater chemistry. Without information regarding the fire history of the Cadillac Brook watershed, researchers may have underestimated the importance of continued N and Hg deposition on this watershed. The burned Cadillac watershed is able to retain much more N and Hg than undisturbed Hadlock because regenerating vegetation (for N) and depleted soil pools (for N and Hg) are recovering from from the effects of the fire.

Objective 2. Compare and contrast the Weathers *et al.* park-scale deposition map for S and N deposition to our intensive small watershed throughfall data.

Key findings: For S as well as Hg, both previous research (Weathers et al. 2000, 2006, Nelson, 2002, Johnson, 2002) as well as data collected during this research found that three key factors influence patterns in variability of atmospheric deposition across Acadia's landscape: vegetation type, elevation and canopy coverage. Canopy coverage per se could not be estimated meaningfully in the previous studies, but in the CART modeling exercise described here shows promise in quantifying the importance of canopy structure in influencing deposition. The Weathers et al. (2006) LAND Mod deposition model is an empirically based regression model that is applied to GIS available data layers to predict deposition over the ACAD landscape. The (GIS-available) drivers of deposition for this model are vegetation type and elevation. "Hot" and "cold" spots of deposition across the ACAD (and GRSM) landscapes were identified using this model. Validation of the Weathers et al. model showed that the model overpredicted deposition for low elevation (low deposition) regions and underpredicted for high elevation (high deposition) regions (Weathers et al. 2006). A preliminary comparison of the LANDMod with TF data collected in the two watersheds suggested that, for particular TF collection

sites, the LANDMod overpredicted deposition compared to these measurements. More analogous to the Weathers et al. (2006) STATMod, we developed a complementary approach, a CART model, that uses local data on canopy-openenness, vegetation type and elevation as the primary drivers of deposition. A preliminary comparison of LANDMod results to the CART model showed better correspondence. Further comparisons and validation exercises are necessary to explore the comparability and utility of these various approaches to deposition mapping.

Management implications. Although models performed differently from each other and over- or under-predicted deposition of S, the factors influencing deposition in each case were the same. Thus, managers can reasonably expect areas with multi-layered mixed vegetation, coniferous vegetation, and high elevation sites to be hotspots of S deposition at Acadia National Park. The results of this project provide another line of evidence supporting the hotspot maps created by Weathers et al. (2006).

Objective 3. Scale the deposition model for S to the entire Park for other analytes, especially Hg [Section 3.3, Section 3.4]. We also evaluate the importance of litterfall Hg deposition [Section 3.7].

Key findings. We found that atmospheric deposition of major ions and Hg was complex, and was the result of spatial and temporal (i.e., seasonal) patterns in weather and deposition. Deposition of Hg and S were similar, with the highest concentrations in summer, lowest concentrations in winter, and similar enhancement patterns with respect to the key landscape factors described above. We modeled Hg deposition across the entire park, based on the results of the CART analysis. Despite our relatively large data set, the model was limited by the number of data points and canopy openness was the only important factor in the model. Modeled deposition of Hg was greatest in areas that were heavily forested, such as the southern end of the east side of MDI. Litterfall Hg flux was similar in magnitude to throughfall flux, and did not vary with vegetation type. This overall result, however, masks the fact that concentrations of Hg in coniferous litter were higher, but litterfall rates were lower and uniformly distributed throughout the year. Deciduous litter had lower Hg concentrations but higher total litterfall, with an obvious high rate of litter Hg delivery to the soil following senescence in the fall.

Management implications. At heavily forested, coniferous sites at Acadia National Park, Hg deposition is likely to be approximately two times that reported in wet-only deposition at the MDN site. Although direct linkages between atmospheric deposition and biota have not yet been defined, recent amphibian Hg data suggest that higher loading to these types of landscapes may translate to higher burdens in biota (Bank, 2005). Further, Acadia appears to receive more Hg deposition in winter than some other U.S. sites, perhaps simply due to relatively large winter precipitation events. Much of the Hg deposited in the northeastern U.S. is derived from long range transport of air masses, not from management activities inside park boundaries. But management of vegetation community composition and structure will have clear consequences for ecosystem contaminant exposure.

Objective 4. Use a field season of stream chemistry to determine whether modeled deposition loading translated directly to stream water quality. A corollary objective was to coordinate legacy datasets into an Acadia stream chemistry database. This database provided background data for this study and was transferred to the Park and to web-based data repositories to enhance access [Section 3.5, Section 3.6].

Key findings. We surveyed major ion chemistry and Hg streams across the Park, some of which had not been sampled since the 1980s (Kahl *et al.*, 1985), and coordinated key stream water quality data sets into a single database. Streams with the highest SO_4 concentrations were in the unburned areas of the park, similar to high deposition zones. Streams with the highest Hg concentration were in the northeast quadrant of MDI, and were typically in low-lying areas. The two highest stream Hg concentrations were in streams influenced by large wetlands. The data suggest that future research should evaluate the role of wetlands in mediating Hg transport from deposition to streams. Although deposition of Hg and S appears to be driven by similar landscape factors (elevation, vegetation type and structure), further research will be necessary to determine which factors drive Hg in streams across the park.

Management implications. In addition to continuous long-term monitoring, spatial variability can be characterized by snapshots of stream chemistry across the park. The 20-year re-sampling of these streams provides a database that will be used to establish conditions and stressors to Acadia's resources (2007). Without these long-term and periodic measurement programs it would be all but impossible to determine ecosystem changes over time.

Objective 5. Though not an original proposed objective, each research watershed and individual site was logged with a GPS unit and translated into GIS (Geographic Information Systems) layers that contained detailed site characteristics.

Key products. Sampling points from legacy datasets – previously only available on a single hard-copy map – were also hand-digitized and migrated to GIS. These data were transferred to the NPS at Acadia for future use by other researchers.

Management implications. Site names and coordinates from the database can be used to select sites for future research projects in the park, in order to best take advantage of available data and determine temporal trends.

5. Future Research Directions

This research project provides baseline data for future research, and highlighted several new research questions:

- What is the role of winter deposition of major ions and Hg? This question is currently under investigation by Nelson et al. and was developed directly from this project. The team is investigating the seasonal and spatial patterns of Hg and major ions in winter in these long-term watersheds at Acadia. The results from the winter deposition study are also being compared to growing-season measurements, and develop a conceptual model for atmospheric deposition.

- How important are wetlands in Hg transport and cycling? Future research could build on the existing Hg stream survey and evaluate the role of wetland extent, wetland type, and proximity to a better understanding of Hg exposure and methylation processes.

- What are the characteristics that influence retention of N (and Hg) following fire? Does fire intensity play a role? Future research could also evaluate the difference in N and Hg retention following other types of disturbance, such as forest cutting or windthrow.

- What are the sources of chemical components in deposition? Back trajectory analyses could be used, in conjunction with our throughfall database, to determine whether there are patterns in air mass trajectories that coordinate with concentration of solutes.

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Table 1. Monthly mean temperature and precipitation for Acadia National Park, Maine, September 1982-November 2003. Daily surface data collected by the National Climatic Data Center as obtained from G. Zielinski, University of Maine.

	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Mean temperature (°C)	-5.7	-4.4	-0.3	5.8	11.9	17.2	20.1	19.8	15.4	9.3	3.6	-2.5
Mean maximum temperature (°C)	-0.2	1.1	4.9	11.4	18.2	23.5	26.2	25.8	21.0	14.5	8.2	2.6
Mean minimum temperature (°C)	-11.2	-10.0	-5.4	0.3	5.6	10.9	13.9	13.7	9.7	4.2	-1.1	-7.5
Precipitation* (cm)	13.3	11.0	14.0	12.1	11.6	9.3	8.6	7.0	10.8	11.9	17.1	12.7
Snow (cm)	48.7	35.4	40.6	11.3	0.1	0.0	0.0	0.0	0.0	0.7	9.2	29.5

* includes melted frozen precipitation

Table 2. Streamflow statistics for two gauged streams at Acadia National Park by calendar year. Streamwater stage monitoring began in April 1999 (Cadillac) and May 1999 (Hadlock), in cubic feet per second (cfs). Discharge is calculated from established relationships with stage and stream channel morphometry. More information, instantaneous data, and streamflow statistics are available on the World Wide Web at http://waterdata.usgs.gov/me/nwis/. Study streams are identified as sites 01022835 (Cadillac Brook) and 01022860 (Hadlock Brook).

Year	**Annual Mean (cfs)**		**Peakflow (cfs)**	
	Cadillac Brook	Hadlock Brook	Cadillac Brook	Hadlock Brook
2000	0.29	0.53	15	29
2001	0.22	0.32	17	49
2002	0.35	0.55	22	71
2003	0.40	0.69	32	78

Table 3. Discharge-weighted chemistry for Cadillac Brook and Hadlock Brook watersheds for calendar years 1999-2003. Numbers in parentheses are sea-salt corrected.

	1999		2000		2001		2002		2003	
	Cadillac	Hadlock	Cadillac	Hadlock	Cadillac	Hadlock	Cadillac	Hadlock	Cadillac	Hadlock
Equilibrated pH	5.86	5.48	5.89	5.45	5.98	5.51	6.11	5.18	5.63	5.54
ANC (μeq/L)	11.6	5.0	9.1	4.7	11.2	6.3	10.8	-0.4	7.0	6.7
Ca (μeq/L)	56.8 (50.4)	62.9 (55.9)	49.4 (43.3)	60.7 (53.9)	44.9 (40.0)	46.5 (41.8)	53.9 (47.2)	45.8 (40.4)	49.3 (43.1)	47.3 (43.0)
Mg (μeq/L)	33 (-6.5)	32.7 (-3.7)	32 (0.5)	36.7 (1.4)	28.2 (2.9)	29.6 (5.4)	35.1 (0.3)	31.9 (4.3)	30.3 (-1.6)	26.7 (4.6)
K (μeq/L)	6.4 (2.7)	7 (3.5)	5.7 (2.7)	6.7 (3.2)	3.4 (1.0)	4.7 (2.4)	4.7 (1.3)	7.5 (4.8)	10.4 (7.3)	5.7 (3.5)
Na (μeq/L)	179 (5.6)	185 (24.1)	166 (26.4)	183 (26.7)	142 (30.1)	145 (38.0)	165 (11.2)	148 (25.9)	144 (3.8)	128 (29.8)
Al (μmol/L)	2.8	6.9	4.3	10	3.8	9.2	3.7	11	7.0	11
NH_4 (μeq/L)	0.6	0.7	3.1	2.8	1.0	1.3	0.5	0.8	1.7	1.7
Si (μmol/L)	73	88	64	78	57	62	76	65	63	83
DOC (μmol/L)	136	256	194	323	131	302	151	372	315	415
Cl (μeq/L)	206	187	162	182	130	124	179	142	162	127
NO_3 (μeq/L)	0.3	5.1	0.8	7.5	0.1	5.9	0.2	9.3	0.1	2.1
SO_4 (μeq/L)	73.2 (51.9)	97.2 (77.9)	77.5 (60.7)	95.0 (76.2)	72 (58.5)	84.7 (71.9)	66.2 (47.7)	78.9 (64.3)	56.7 (40.0)	73.1 (60.0)
Total Hg (ng/L)	0.59	1.29	1.17	2.14	0.70	1.48	0.44	4.05	0.93	3.36
MeHg (ng/L)	-	-	0.04	0.04	0.04	0.04	-	-	-	-

Table 4: Annual fluxes of major ions and Hg in Cadillac and Hadlock Brook streamwater, 1999-2003. Hadlock Brook watershed continues to export more NO_3 and Hg than Cadillac Brook watershed. Interannual variability was reflected in water and ion flux, with droughts in 2001 and 2002.

	Water Year	Water	ANC	H^+	Ca	Mg	K	Na	Cl	NO_3	SO_4	Al	DOC	Total Hg
	Oct 1-Sep 30	*x10^6, liters/yr*					*eq/ha/yr*					*mol/ha/yr*		*ug/m^2/yr*
Cadillac	1999[+]	56.4	33	1	128	74	13	331	426	0.9	124	8	218	0.076
Brook	2000	261	91	12	454	285	40	1552	1608	3.9	625	27	928	0.386
Watershed	2001	251	113	9	398	250	31	1253	1170	3.2	587	31	999	0.476
	2002	241	127	5	363	228	32	1099	1063	1.4	579	28	804	0.275
	2003	310	156	6	433	280	35	1283	1182	0.5	676	35	1101	0.404
Hadlock	1999[+]	81.8	33	18	161	76	13	329	400	5.38	180	10	357	0.129
Brook	2000	472	88	33	712	396	73	1947	2104	81.4	948	65	1878	0.989
watershed	2001	372	111	21	474	261	39	1282	1093	40.3	747	66	2141	1.261
	2002	357	157	20	524	285	42	1251	1201	58.1	730	55	1563	1.120
	2003	532	247	11	753	401	52	1692	1513	48.9	1029	72	2181	1.251

[+] Fluxes for water year 1999 were from May 1 - Sept. 30

Table 5. National Atmospheric Deposition Program (NADP) and Mercury Deposition Network (MDN) precipitation weighted mean (a) concentrations of major ions and total Hg, pH and specific conductance and (b) annual deposition of major ions and Hg, and precipitation depth for Acadia National Park – McFarland Hill (Site ME98), by calendar year. Hg data were not available (n/a) for all of calendar year 2004 at the time of publication.

Table 5a

Year	**Ca**	**Mg**	**K**	**Na**	**NH_4**	**NO_3**	**Cl**	**SO_4**	**pH**	**Specific Conductance**	**Total Hg**
				mg/L					SU	µs/cm	ng/L
1999	0.06	0.086	0.031	0.764	0.09	0.67	1.32	0.93	4.74	15.0	9.3
2000	0.08	0.105	0.038	0.932	0.13	0.93	1.49	1.22	4.61	19.4	9.8
2001	0.06	0.047	0.019	0.416	0.12	0.95	0.75	1.01	4.63	15.7	11.8
2002	0.05	0.082	0.029	0.719	0.12	0.65	1.30	0.91	4.80	14.5	10.2
2003	0.05	0.053	0.020	0.458	0.09	0.56	0.83	0.76	4.80	12.3	8.1
2004	0.06	0.051	0.020	0.425	0.13	0.71	0.79	1.07	4.65	15.0	n/a

Table 5b

Year	**Ca**	**Mg**	**K**	**Na**	**NH_4**	**NO_3**	**Inorg. N**	**Cl**	**SO_4**	**H^+ (Lab)**	**Precip. Depth**	**Hg**
					kg/ha						cm	µg/m^2/yr
1999*	0.82	1.155	0.416	10.264	1.16	8.97	2.92	17.79	12.51	0.25	134.34	7.9
2000*	1.08	1.351	0.489	11.988	1.67	12.01	4.01	19.14	15.74	0.32	128.63	8.6
2001	0.39	0.297	0.120	2.632	0.73	5.98	1.92	4.74	6.38	0.15	63.26	4.6
2002*	0.85	1.297	0.459	11.368	1.87	10.29	3.78	20.59	14.32	0.25	158.11	7.9
2003	0.59	0.683	0.258	5.899	1.20	7.21	2.56	10.74	9.79	0.20	128.80	7.1
2004	0.59	0.546	0.214	4.547	1.36	7.59	2.77	8.48	11.47	0.24	107.00	n/a

* NADP Data Completion Criterion 4 was <75% for these years; all other Data Completeness Criteria were acceptable.

Table 6. Volume weighted mean chemistry for 29 throughfall collections at Acadia National Park during 1999, 2000, 2001, and 2004, by year. Hg was not sampled in 2001. The bulk collector values were sampled at the McFarland Hill NADP site. SO_4* is marine corrected sulfate.

Watershed	Year	Water *mm*	Equilibrated pH	DOC *mg/L*	Ca	Mg	K	Na	NH_4 *μeq/L*	SO_4	SO_4*	Cl	NO_3	Total Hg *(ng/L)*
Cadillac	1999	60.4	4.77	11.27	30	38	47	113	7.1	62	47	149	26.7	7.6
Hadlock		76.5	4.45	12.98	33	43	43	151	14.3	76	56	188	42.6	10.3
Cadillac	2000	68.2	4.81	7.66	16	17	28	43	4.2	45	40	51	15.4	11.6
Hadlock		65.4	4.64	11.00	19	22	34	56	9.1	57	51	64	22.2	14.4
Bulk collector		40.0	4.63	2.80	4	3	4	16	6.0	35	34	16	12.0	6.8
Cadillac	2001	83.7	4.76	10.31	16	17	28	37	3.8	43	38	49	17.0	
Hadlock		86.5	4.66	13.75	27	27	41	54	6.2	58	51	69	29.0	
Bulk collector		69.3	5.18	6.53	4	3	3	12	22.9	26	24	13	9.6	
Cadillac	2004	82.2	4.88	8.91	17	18	31	40	2.4	40	35	49	8.8	14.1
Hadlock		66.8	4.83	12.27	21	20	43	46	3.7	50	44	59	8.8	15.6
Bulk collector		79.7	4.47	4.88	4	5	1	18	3.8	27	25	20	10.2	7.2

Table 7. Annual enhancement of deposition in throughfall as compared to wet-only deposition for paired watersheds at Acadia National Park. Enhancement ratios were determined using throughfall and NADP data from synchronized sampling periods in 1999 and 2000. Ratios were determined for each vegetation type. Data from wet-only samplers in each watershed were compared to NADP deposition as a quality assurance check.

Vegetation	Ca^{2+}	Cl^-	H^+	K^+	H_2O	Mg^{2+}	Na^+	NH_4^+	NO_3^-	SO_4^{2-}
Hadlock: NADP										
Open/Bulk	2.94	4.26	4.96	20.2	0.92	5.08	4.35	1.15	1.52	2.05
Scrub	1.22	1.46	4.20	9.26	0.91	1.26	1.53	0.80	0.70	1.22
Deciduous	4.27	2.53	1.57	57.6	0.85	5.22	2.43	1.03	0.71	1.50
Mixed	6.63	6.83	3.63	77.8	0.84	9.31	6.83	1.88	1.85	2.55
Coniferous	6.78	7.09	4.66	58.1	0.85	9.23	7.27	2.03	1.99	2.74
Cadillac: NADP										
Open/Bulk	1.22	1.68	3.69	9.0	0.84	1.89	1.95	0.42	0.73	1.15
Scrub	2.74	3.31	4.26	16.5	0.90	4.07	3.51	0.63	0.92	1.51
Deciduous	4.51	2.86	2.30	58.0	0.83	4.91	2.71	0.50	0.68	1.56
Mixed	6.21	5.96	2.34	70.2	0.73	8.49	5.83	0.71	1.29	2.10
Coniferous	5.57	5.31	3.71	42.1	0.93	7.95	5.77	0.90	1.27	2.22
Watershed wet-only: NADP										
Open*	0.93	1.80	1.10	1.87	1.02	1.10	1.87	1.50	1.10	1.13

* Sites did not adhere to NADP standards (distance from the sampler to nearby vegetation must be at least equal to the height of the vegetation) because it was not feasible to remove vegetation surrounding these sites in the park.

Table 8. Throughfall enhancement of SO_4, Cl, and Ca for this study and sites in the northeastern U.S. and eastern Canada.

Site	Vegetation Type	SO_4^{2-}	Cl^-	Ca^{2+}
Acadia National Park, ME, USA (This study)	Deciduous	1.5	2.7	4.4
	Coniferous	2.5	6.2	6.2
Bear Brook, ME, USA (Rustad *et al.*, 1994*)	Mixed	1.9	2.5	
Lake Clair, Quebec, CA (Houle *et al.*, 1999b)	Deciduous	1.2	2.2	4.5
	Coniferous	1.4	2.7	4.9
Hubbard Brook, NH, USA† (Likens and Bormann, 1995)	Deciduous	1.7	0.7	3.0
Howland, ME, USA (Johnson and Lindberg, 1992; as reported in Rustad *et al.*, 1994*)	Coniferous	2.0	2.4	

* Rustad et al. (1994) report "wet" and "dry" deposition. We calculated wet+dry/wet and used "canopy mass balance" (throughfall) estimates of dry deposition for comparability between sites.
† Likens and Bormann (1995) report throughfall and bulk (not wet-only) annual fluxes (p. 109), from which these values were calculated.

Table 9. Comparison of throughfall deposition from Cadillac and Hadlock Brook watersheds and bulk deposition measured at National Atmospheric Deposition Program site ME98, McFarland Hill, in our co-located collector. Data are presented in mass per hectare for the entire period sampled in each year, and are directly comparable between sites but not between years. Deposition of major ions and Hg were typically highest at Hadlock Brook watershed, and lowest at the McFarland Hill site, which was non-vegetated. Hg in 1999 was only collected in October and November.

	1999: Aug 1 - Nov 19			**2000: May 1-Nov 16**			**2001: Apr 30-Nov 17**			**2004: May 28-Nov 23**		
	Cadillac	Hadlock	McFarland	Cadillac	Hadlock	McFarland	Cadillac	Hadlock	McFarland	Cadillac	Hadlock	McFarland
Ca (eq/ha)	50.1	74.9	not sampled	83.0	70.4	14.5	46.4	58.3	9.08	70.1	50.4	22.0
Cl (eq/ha)	267	458		274	249	52.8	128	159	28.7	216	161	98.1
Hg ($\mu g/m^2$)	0.57	0.99		5.56	6.19	2.22				3.85	5.11	3.13
H^+ (eq/ha)	58.6	158		151	190	113	86.5	108	57.8	133	121	187
K (eq/ha)	73.7	86.3		140	105	12.1	76.4	86.6	5.77	105	82.4	4.49
Mg (eq/ha)	67.2	108		90.2	76.7	10.2	46.7	59.0	7.62	74.1	50.2	24.4
Na (eq/ha)	206	399		233	222	52.6	95.5	119	25.3	183	136	89.6
NH_4 (eq/ha)	13.5	40.7		25.1	44.9	20.0	11.1	16.3	50.2	16.6	16.1	19.3
NO_3 (eq/ha)	51.3	109		88.2	94.8	39.8	45.7	63.6	21.0	50.8	35.8	51.0
SO_4 (eq/ha)	107	203		241	257	118	117	141	55.9	184	160	136
Water (cm)	15.0	40.6*		51.1	51.3	33.2	30.9	30.1	21.9	49.4	41.6	50.2

* The major difference in water volume between Cadillac and Hadlock in 1999 is attributed to the month of September, which included two extremely large events (one a hurricane). No data errors were found in analyses of the apparent discrepancy.

Table 10. Summary statistics for Hg deposition and concentration at three Mercury Deposition Network (MDN) sites for Jan. 4 2000-Dec. 31 2002. Site WI36: Trout Lake LTER, Wisconsin; Site SC19: Congaree Swamp, South Carolina; Site ME98: Acadia National Park – McFarland Hill, Maine.

	WI36	SC19	ME98	WI36	SC19	ME98
	Deposition (ng/m^2)			Concentration (ng/L)		
Minimum	0.0	0.0	4.2	< DL	0.3	0.3
Maximum	2478.9	1268.0	913.0	39.6	64.0	102.4
Mean	193.2	257.1	157.9	9.6	13.5	10.5

Table 11. Seasonal and annual wet deposition fluxes to three MDN sites during 2000, 2001, and 2002, calculated by summing MDN-reported weekly fluxes. Units for seasonal fluxes are ng/m^2/season and for annual fluxes are ng/m^2/yr. Each season's contribution the annual flux is calculated as a percent for each site.

	Season	**WI 36**		**SC 19**		**ME 98**	
		Flux (ng/m^2)	Percent of Annual Flux	Flux (ng/m^2)	Percent of Annual Flux	Flux (ng/m^2)	Percent of Annual Flux
2000	Winter	637	7.1%	835	8.8%	2362	27.5%
	Spring	1126	12.5%	2257	23.9%	3238	37.7%
	Summer	5895	65.6%	4871	51.6%	2015	23.4%
	Fall	1334	14.8%	1481	15.7%	978	11.4%
	Annual	**8992**		**9444**		**8593**	
2001	Winter	466	5.8%	737	8.2%	849	18.2%
	Spring	2526	31.5%	2555	28.6%	905	19.4%
	Summer	3309	41.2%	3761	42.0%	1857	39.9%
	Fall	1726	21.5%	1894	21.2%	1046	22.5%
	Annual	**8026**		**8947**		**4656**	
2002	Winter	279	2.8%	1470	14.9%	1312	16.6%
	Spring	3202	32.5%	3020	30.5%	3165	40.0%
	Summer	4467	45.4%	2459	24.9%	1902	24.0%
	Fall	1890	19.2%	2939	29.7%	1532	19.4%
	Annual	**9837**		**9888**		**7910**	

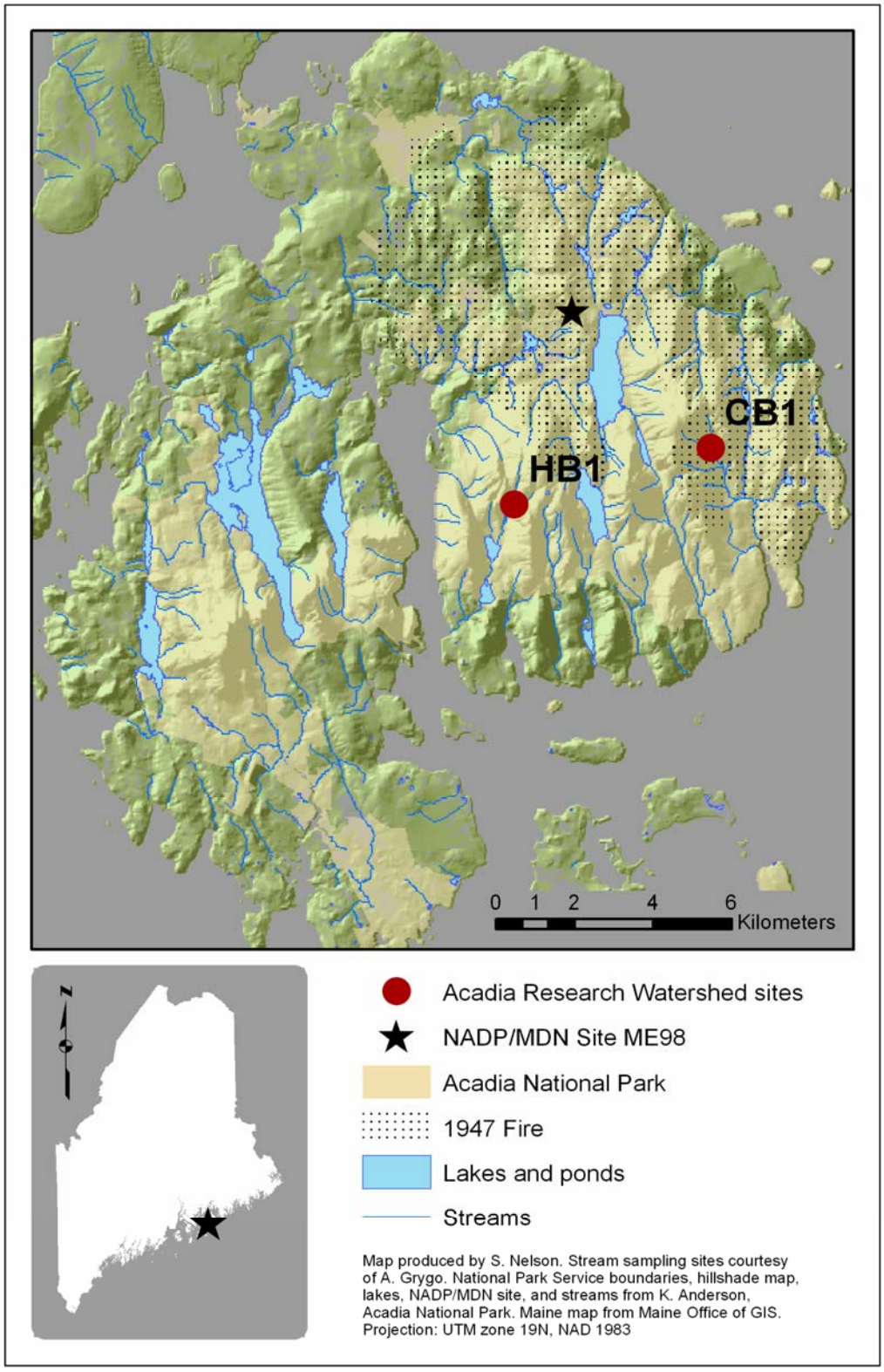


Figure 1. Location of research sites: Hadlock Brook watershed stream sampling site (HB1) and Cadillac Brook watershed stream sampling site (CB1). Area burned in 1947 shown with stippled shading.

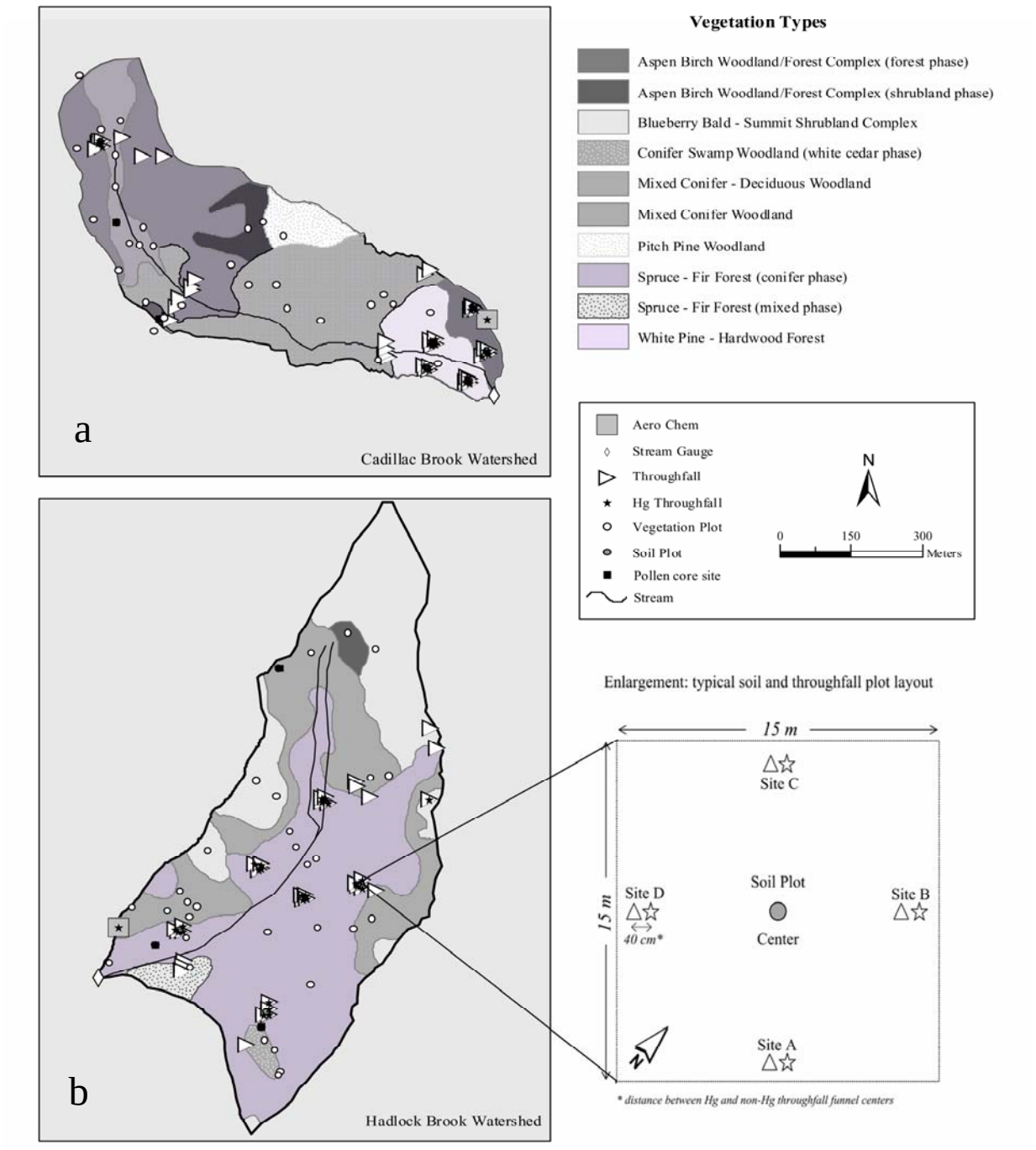


Figure 2. Study watersheds at Acadia National Park: (a) Cadillac Brook watershed, and (b) Hadlock Brook watershed with locations of throughfall and litter collectors, wet-only precipitation collectors, stream discharge gauges, soil plots, Hg soil assay sites, and paleoecological cores; National Park Service – USGS mapping project vegetation classification (Lubinski *et al.*, 2003) for Cadillac Brook watershed and Hadlock Brook watershed is displayed in the background. The inset at right shows the typical soil and throughfall plot layout.

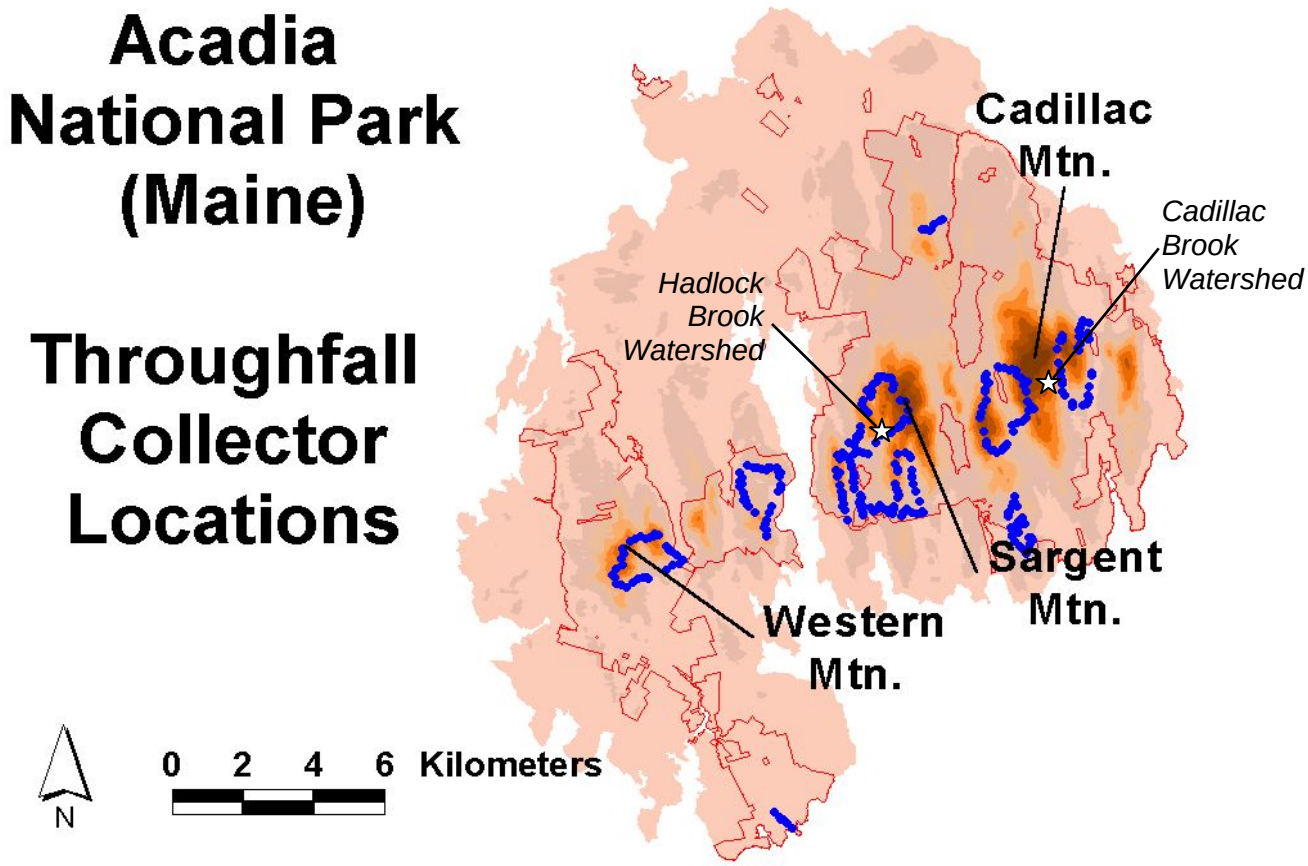


Figure 3. Throughfall sites sampled by Weathers et al. in 2000 (blue dots). Cadillac Brook watershed and Hadlock Brook watershed are shown (stars) for reference.

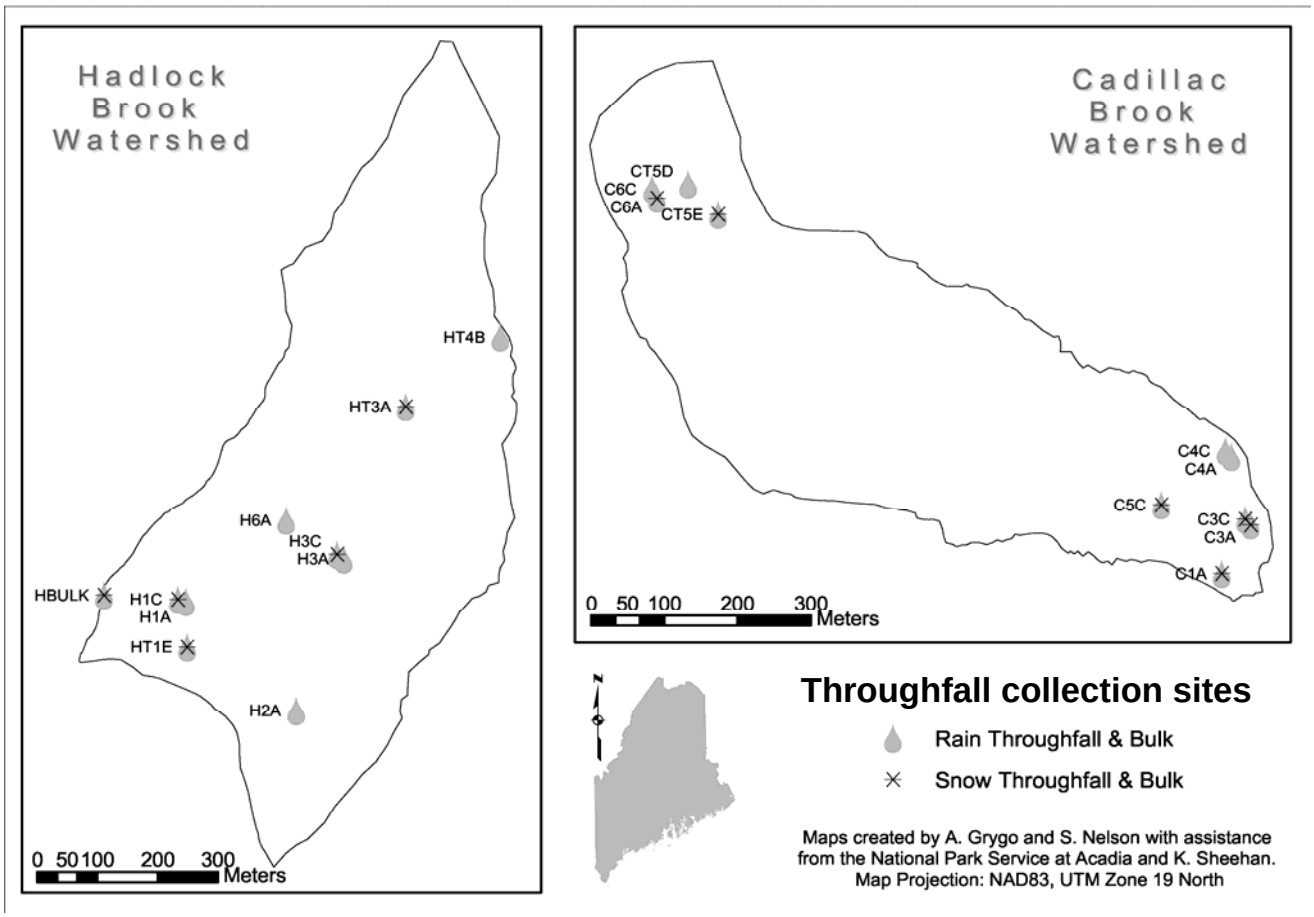


Figure 4. Sample sites for 10-level (snow) and 20-level (rain) throughfall collection, determined using cluster analysis. Not shown: a bulk collector located at McFarland Hill, which allows intercomparison with other research sites.

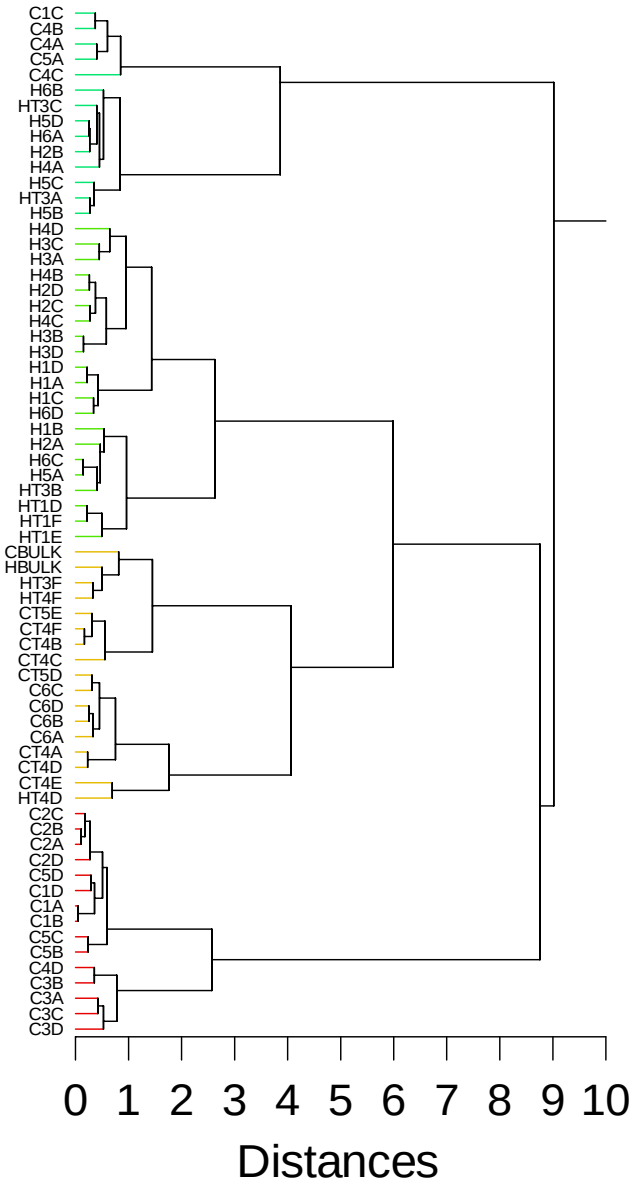


Figure 5. Example dendrogram (cluster tree) resulting from hierarchical clustering using Euclidean distance and Ward's minimum variance linkage method for throughfall Collection 7 (May 2000). In each group, sites are similar with respect to landscape and chemical characteristics.

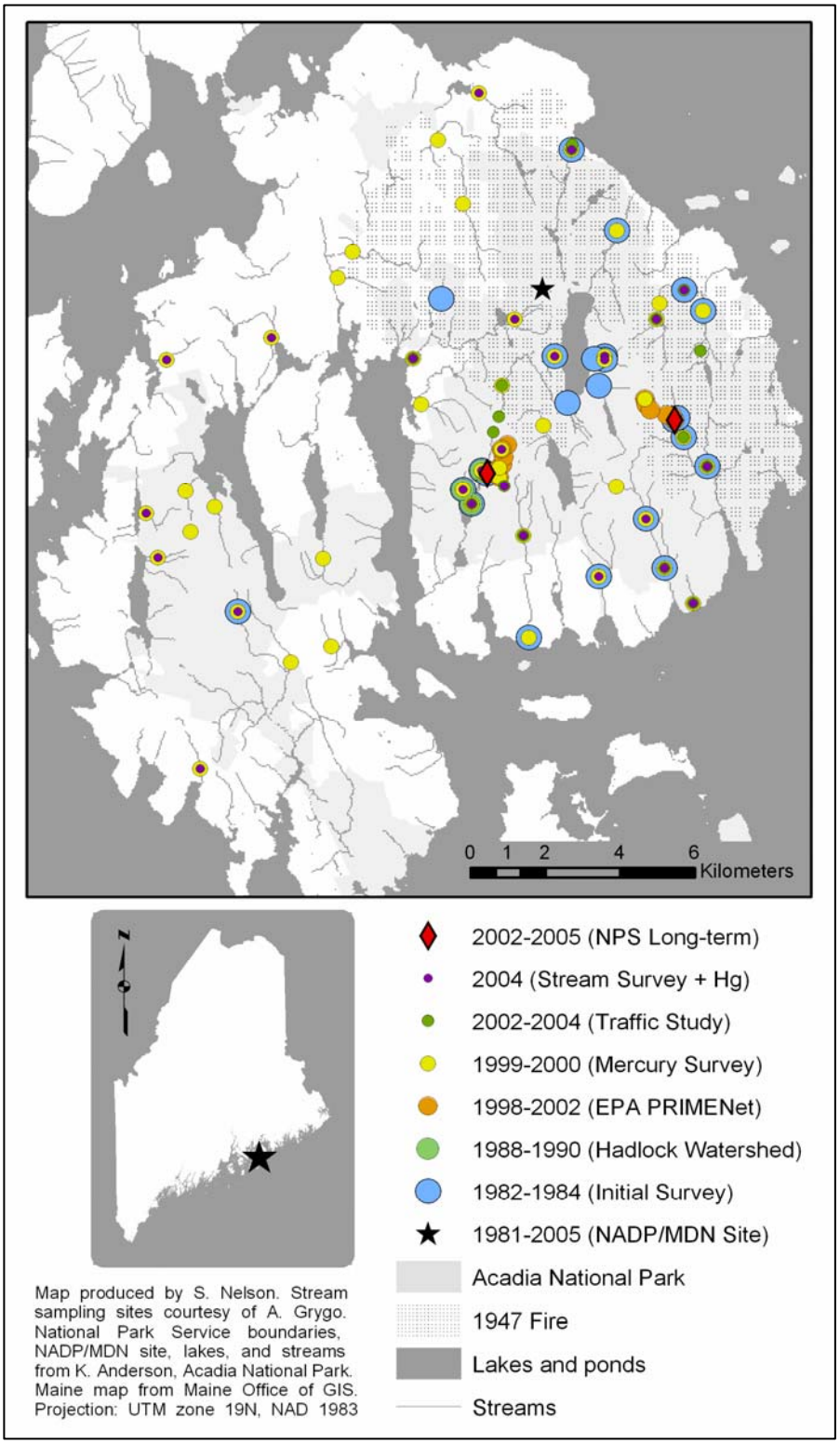


Figure 6. Location of sites that have been sampled in research on streams at Acadia National Park since 1982. Sites sampled for this project are the 2002-2005 NPS Long-term sites, and the 2004 Stream survey & Hg sites. Overlapping dots show sites that have been sampled multiple times as part of multiple projects. These sites all have data represented in the database delivered to NPS.

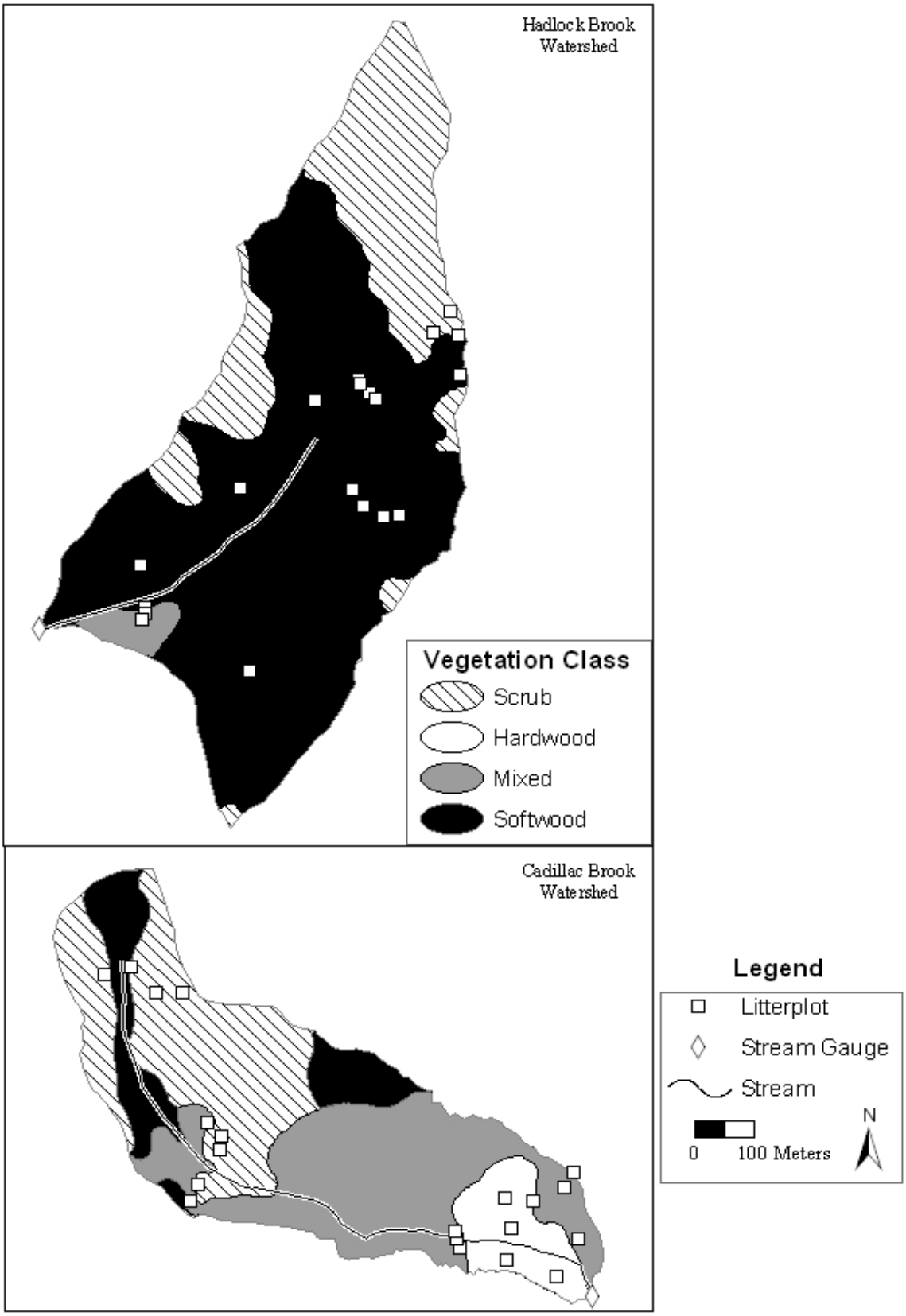


Figure 7. Map of vegetation type distributions and litter sample site locations within the study watersheds, Acadia National Park, Maine.

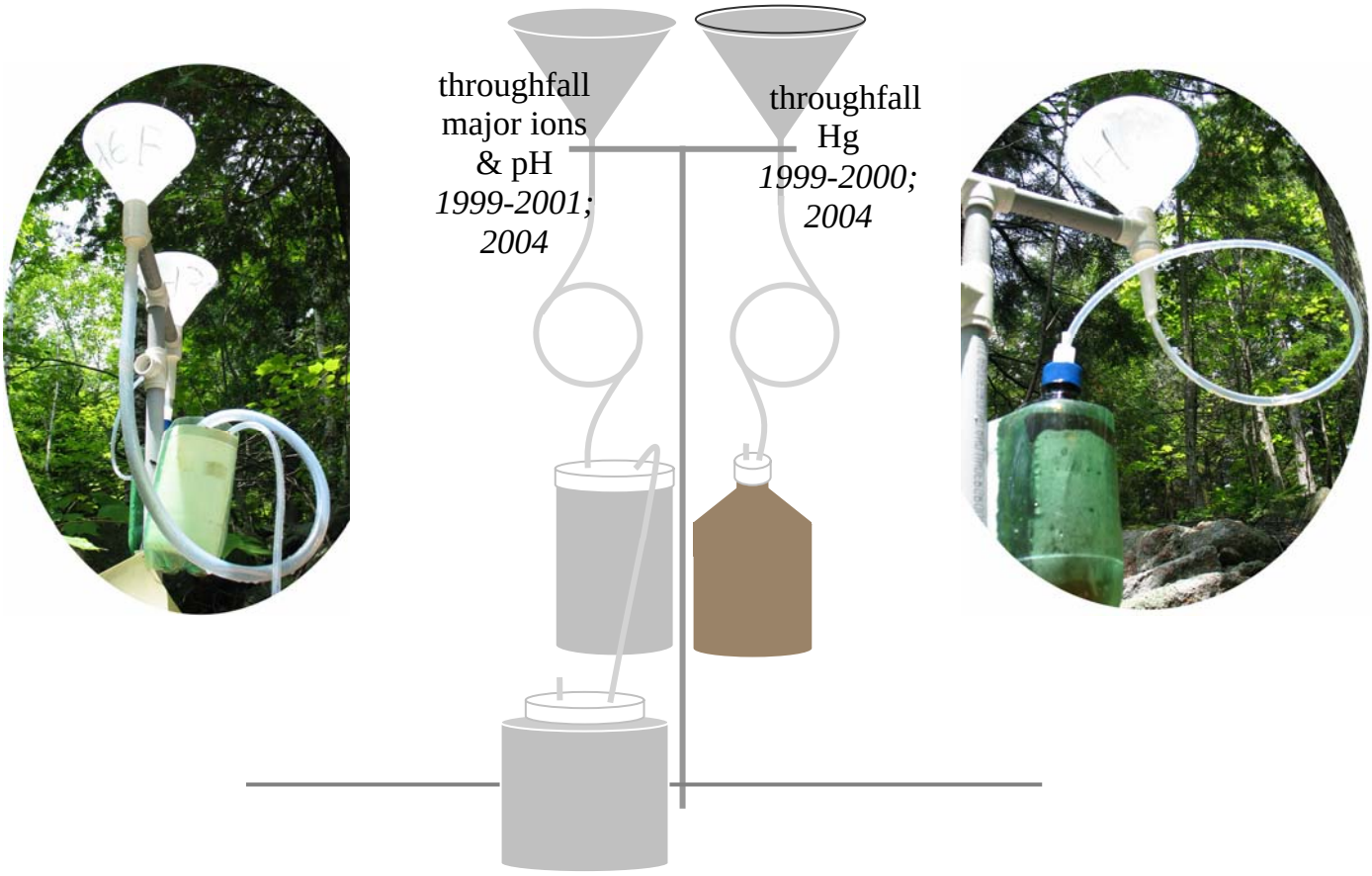


Figure 8. Rain throughfall collector design schematic and photographs of collectors in the field. Left side of collector is constructed of HDPE plastic components for major ion analysis; right side is constructed of borosilicate glass and Teflon components for Hg analysis. Collector design details in Nelson (2002) and Johnson (2002).

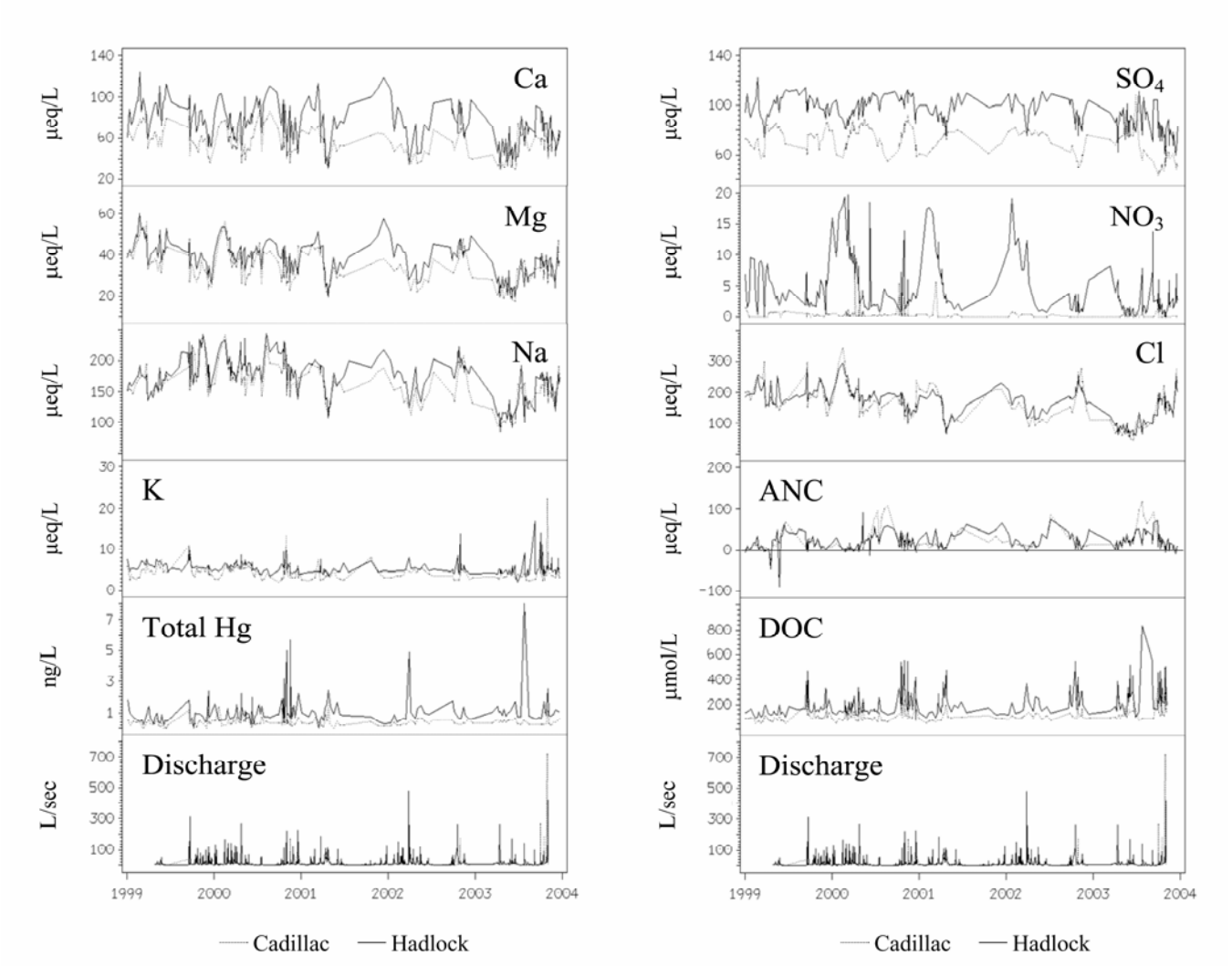


Figure 9. Concentrations of major ions, mercury (Hg), and dissolved organic carbon (DOC) in Cadillac and Hadlock brooks for 1999-2003. Stream discharge is shown at the bottom of each panel.

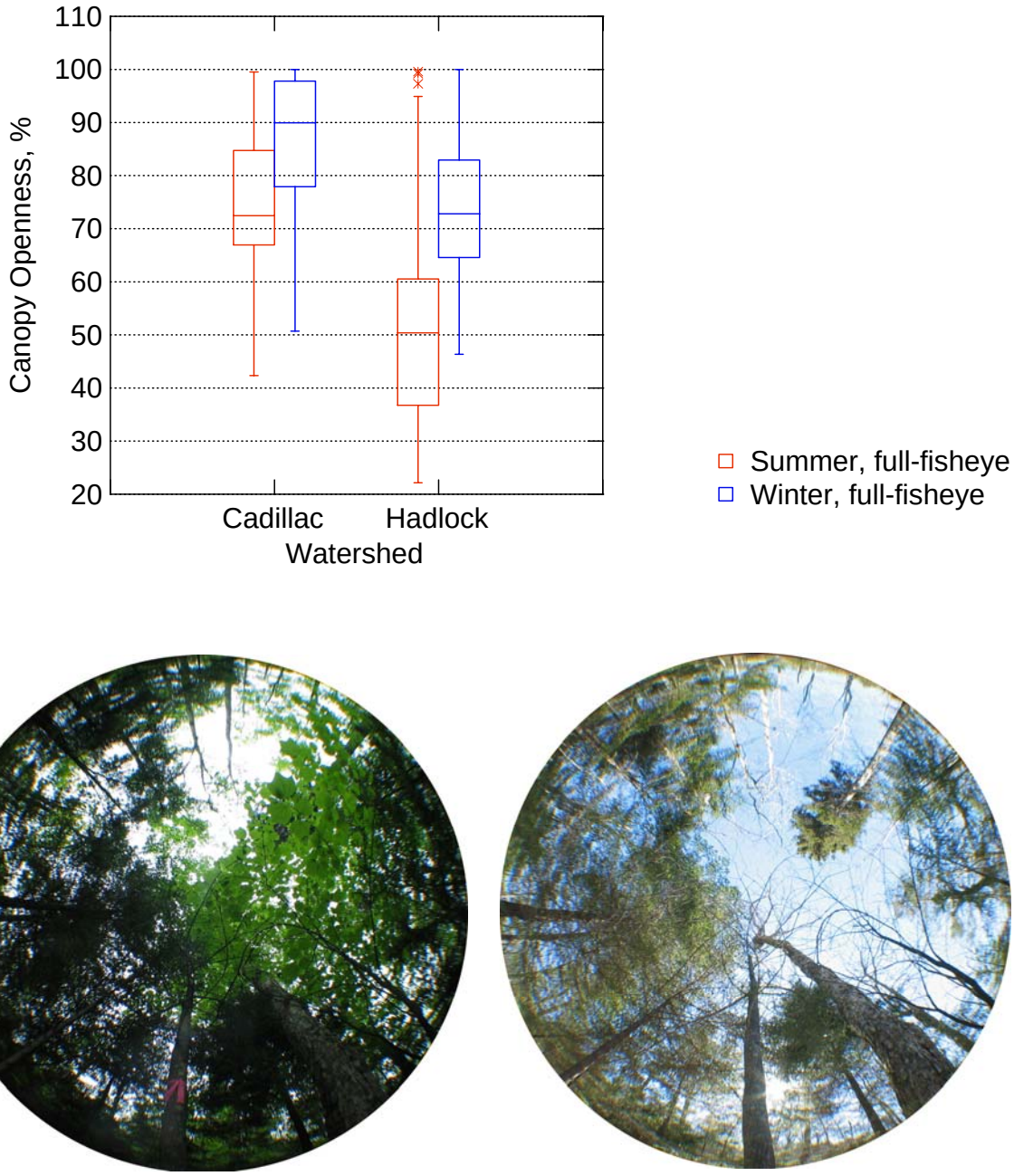
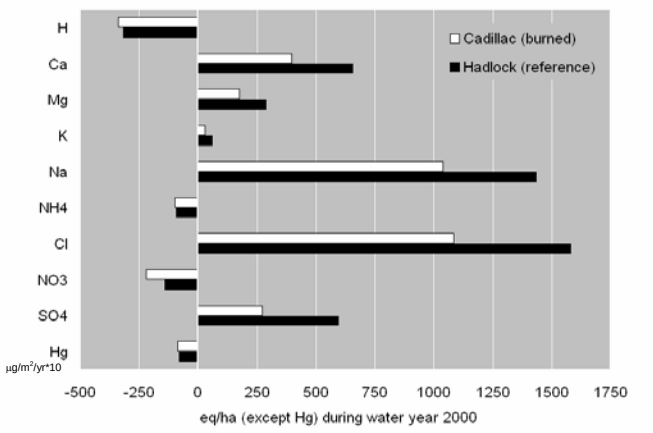
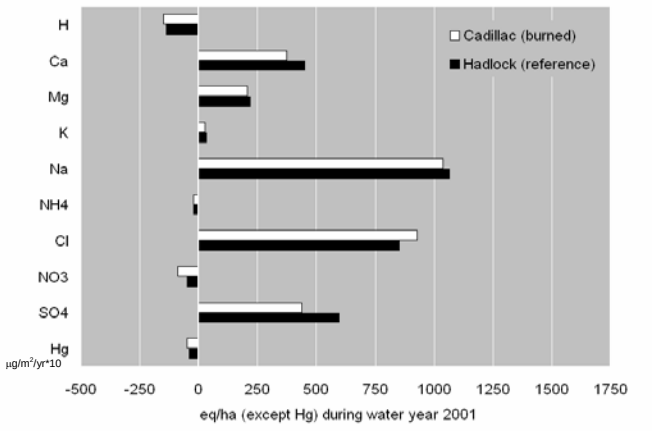
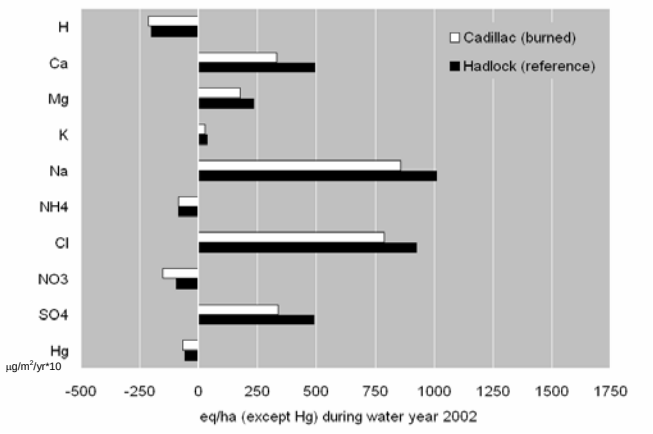


Figure 10. Canopy openness as measured using fisheye digital photography in both summer and winter in the two research watersheds at Acadia National Park. Hadlock Brook watershed had lower openness (more closed canopy) than Cadillac Brook watershed in both summer and winter. Winter openness was greater than summer openness in both watersheds. Photos show an example of the photographs, in this case a summer photo (left) and winter photo (right) of the same site in Hadlock watershed.







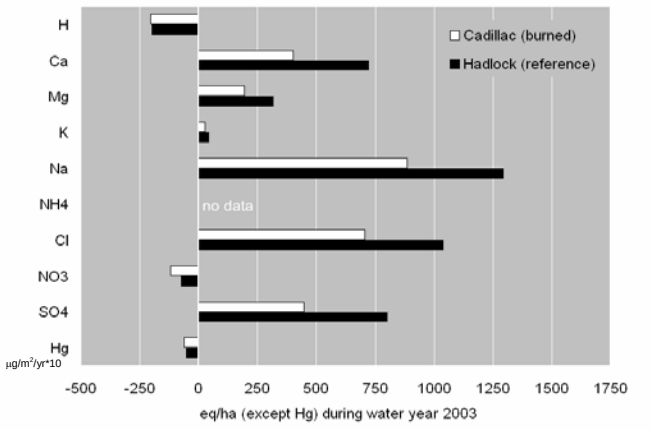


Figure 11. Mass balance (streamwater export minus wet precipitation input) of major ions and mercury (Hg) in the study watersheds for water years 2000-2003. Note that Hg has different units ($\mu g/m^2/yr$) and is multiplied by 10 for graphical display purposes. Positive values indicate net loss from the watershed and negative values indicate net retention. Wet precipitation data from the National Atmospheric Deposition Program (NADP) and Mercury Deposition Network (MDN) for site ME98. Use of wet deposition data explains the net loss of Na and Cl, and the coniferous canopy at Hadlock Brook watershed would account for its greater loss of these ions when dry deposition is not taken into account.

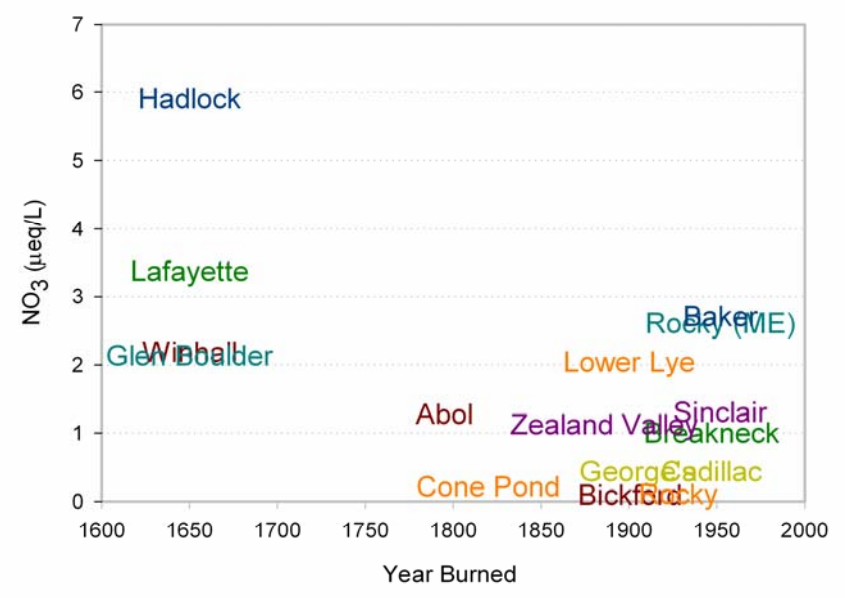


Figure 12. Mean NO_3 concentration in New England streams *versus* estimated year the site burned.The Hadlock (unburned) and Cadillac (burned) sites at Acadia are endmembers of this possible chronosequence. A default date of 1650 was chosen to represent unburned or 'old-growth' sites, for display purposes.

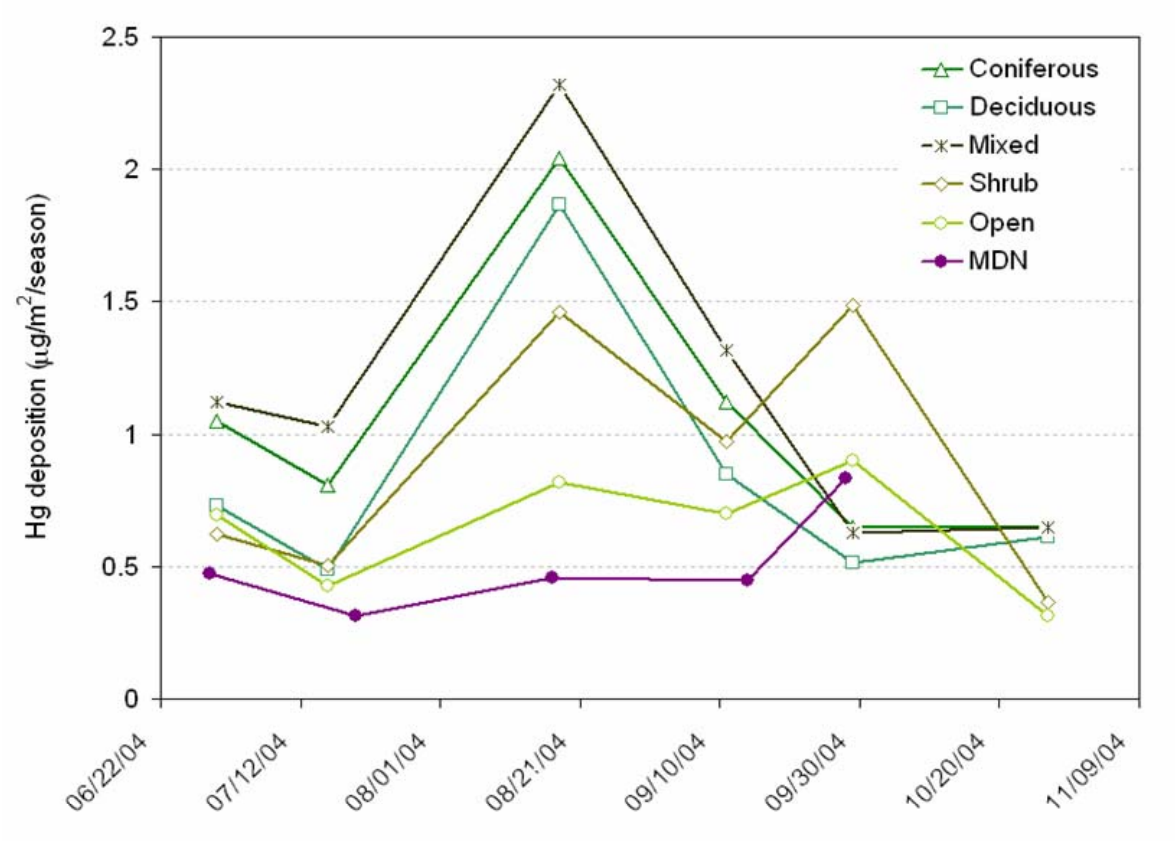


Figure 13. Rain throughfall Hg deposition at Acadia National Park, sampled at 21 sites in 2004. The throughfall data show temporal fluctuation, and follow the general pattern mixed > coniferous > deciduous > shrub/open sites > MDN wet-only deposition.

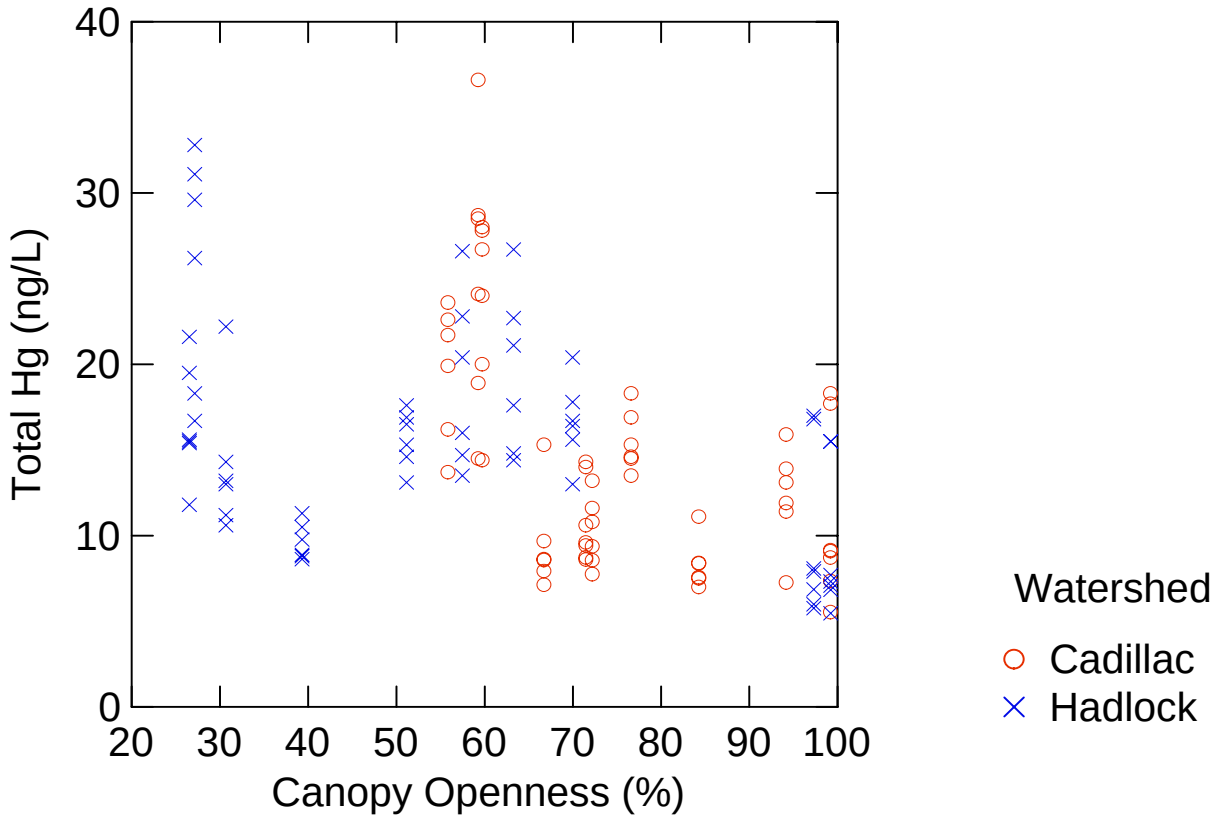


Figure 14. Total Hg in throughfall deposition for 2004, plotted against canopy openness in percent. Sites with low values for canopy openness are typically conifer or mixed sites, and sites with high values for canopy openness are typically scrub/shrub or non-vegetated sites. Openness tends to be lower overall in Cadillac Brook watershed.

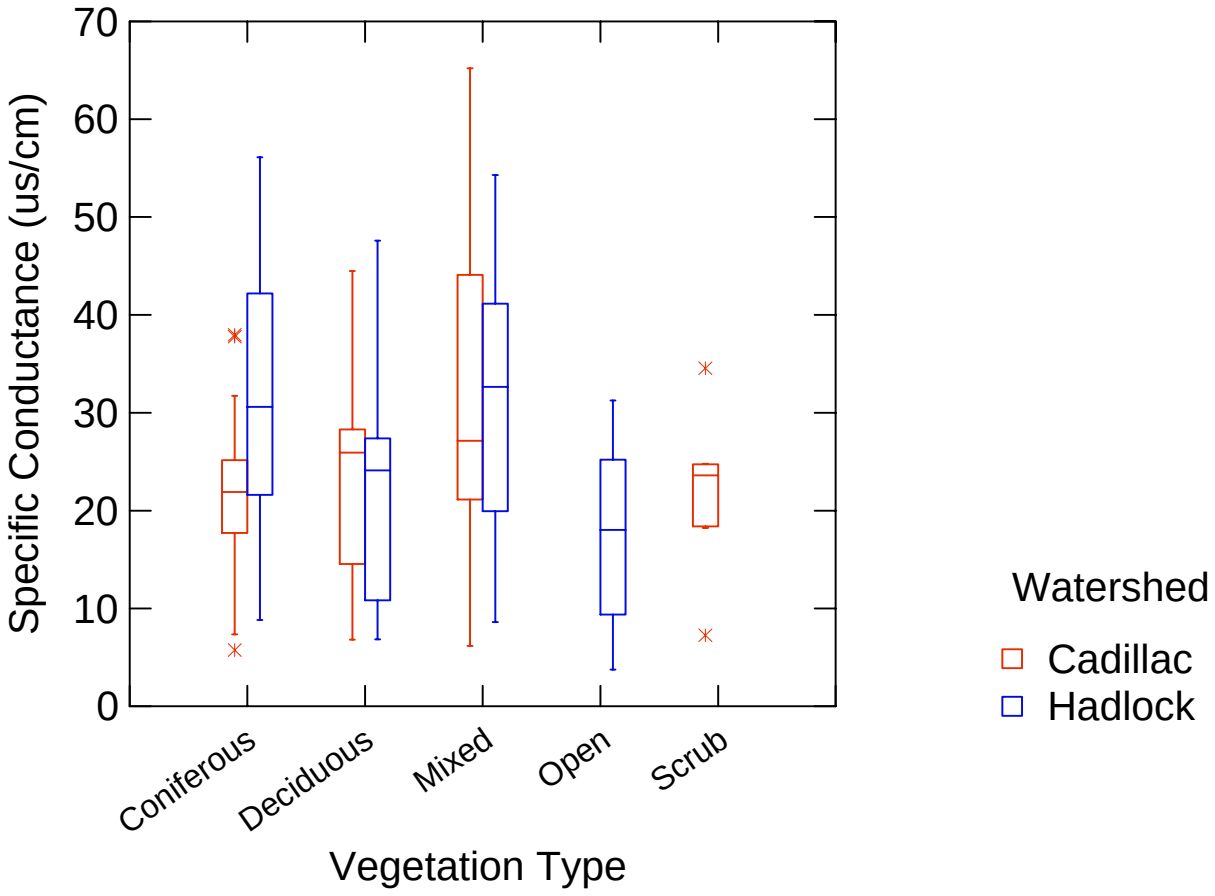


Figure 15. Box plot showing specific conductance, highly correlated with all major ions (except NO_3) and DOC in throughfall deposition for 2004, plotted against vegetation type at each throughfall site. Median values are denoted by the horizontal lines inside boxes. Deposition tended to be higher at mixed and coniferous sites than other vegetation types, and slightly higher at Hadlock Brook watershed conifer and mixed sites than at the same types of sites Cadillac Brook.

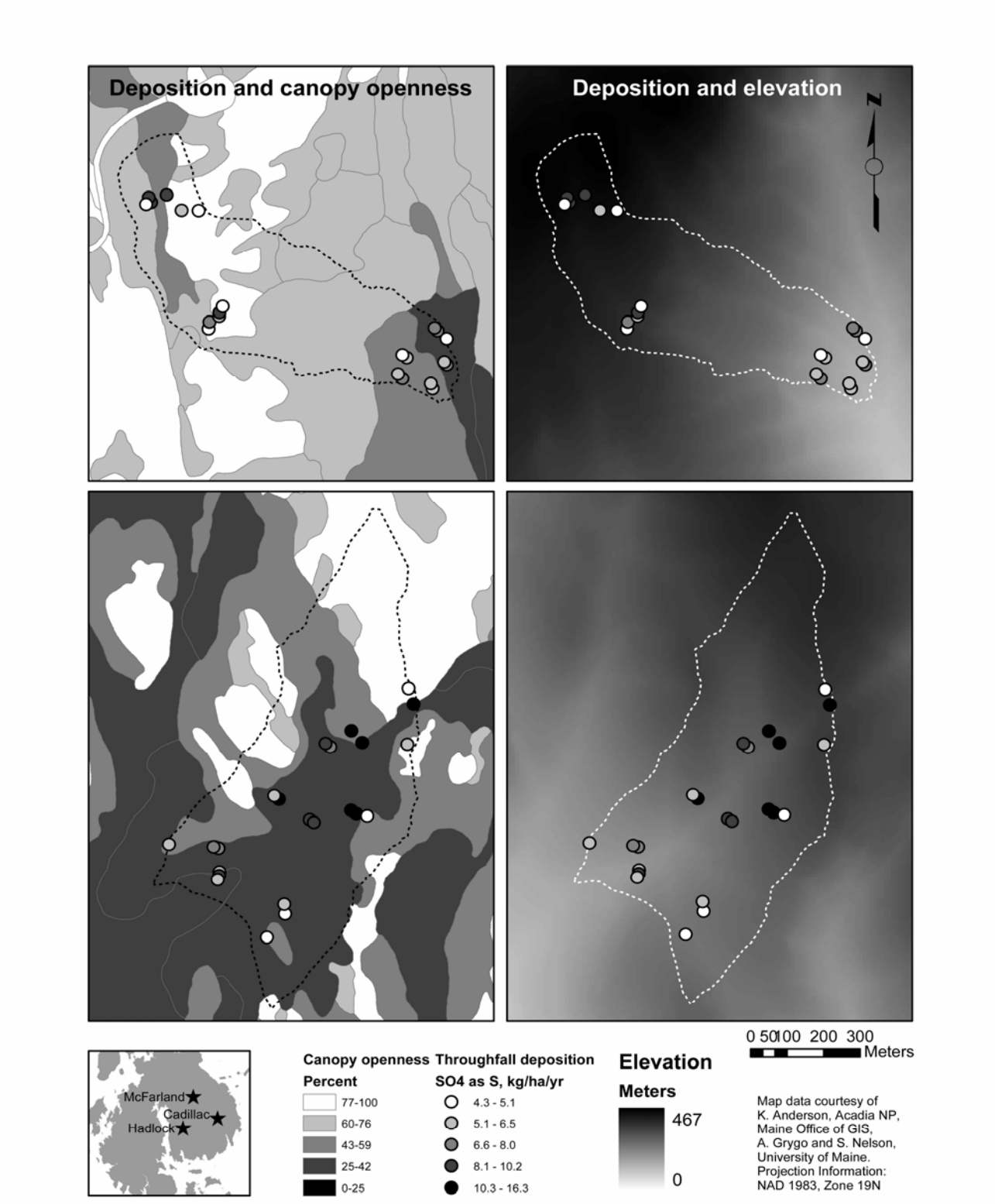


Figure 16. Relationship between deposition of S and (left) canopy openness (as determined from regression with canopy height) and (right) elevation. Darker dots indicate higher deposition; darker zones for openness or elevation indicate the expectation of higher deposition. While many observed values relate to each landscape characteristic, others indicate heterogeneity at these sites and the need for multivariate statistical methods.

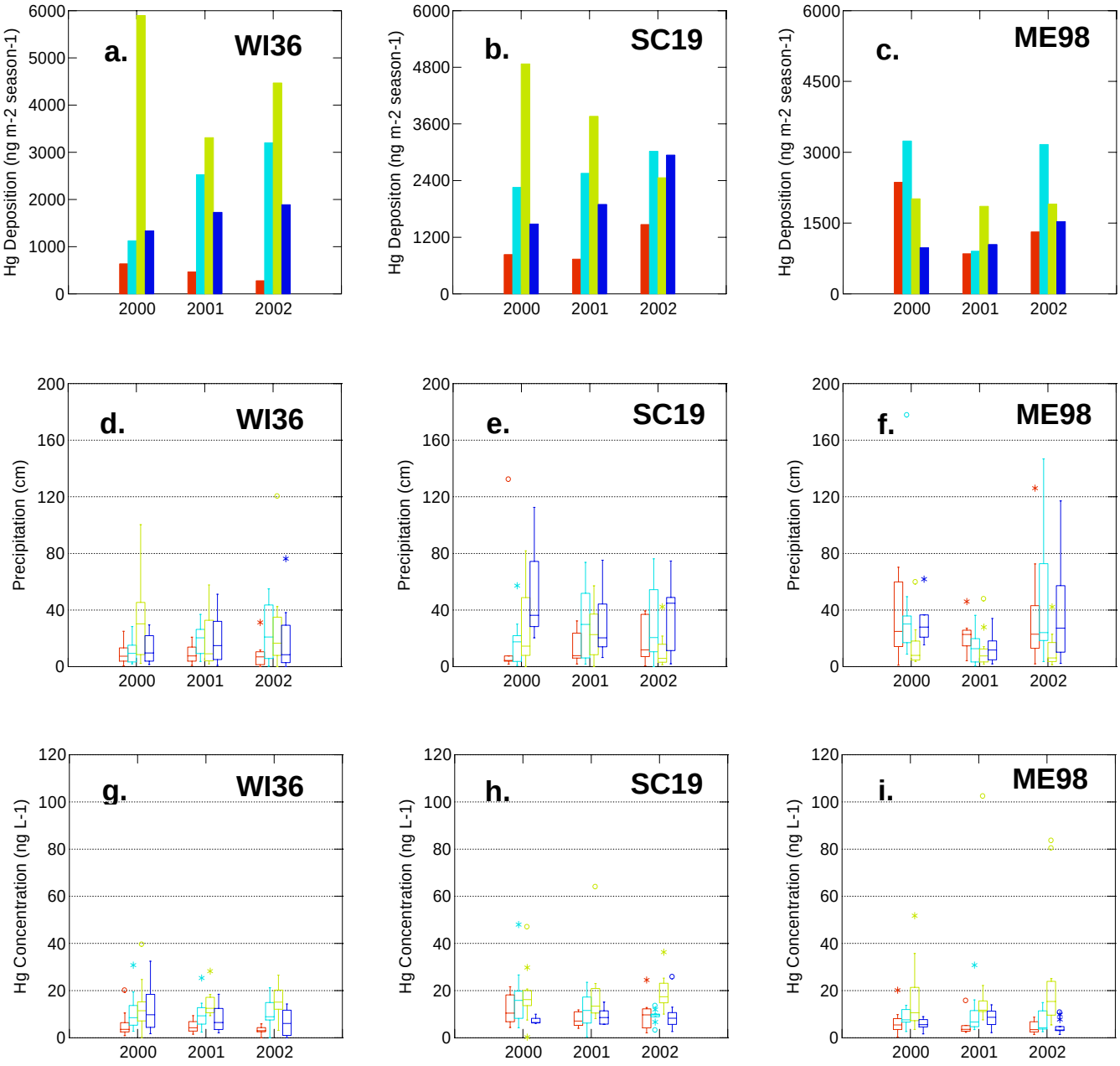


Figure 17. 2000-2002 Hg deposition as total seasonal flux (a.-c.), precipitation amounts (d.-f.) and volume-weighted concentration (g.-i.) for three MDN sites: WI36 (Trout Lake LTER), SC19 (Congaree Swamp) and ME98 (Acadia National Park), by season and year. Plots d-i are box plots, where the center vertical line marks the median of the sample. The length of each box shows the range within which the central 50% of the values fall (interquartile range), with the box edges at the first and third quartiles. The whiskers show the range of values that fall within 1.5 times the interquartile range. Values between the inner fences (1.5 times interquartile range) and outer fences (3 times interquartile range) are plotted with asterisks. Values beyond the outer fences, called far outside values, are plotted with empty circles.

Season
- Winter
- Spring
- Summer
- Fall

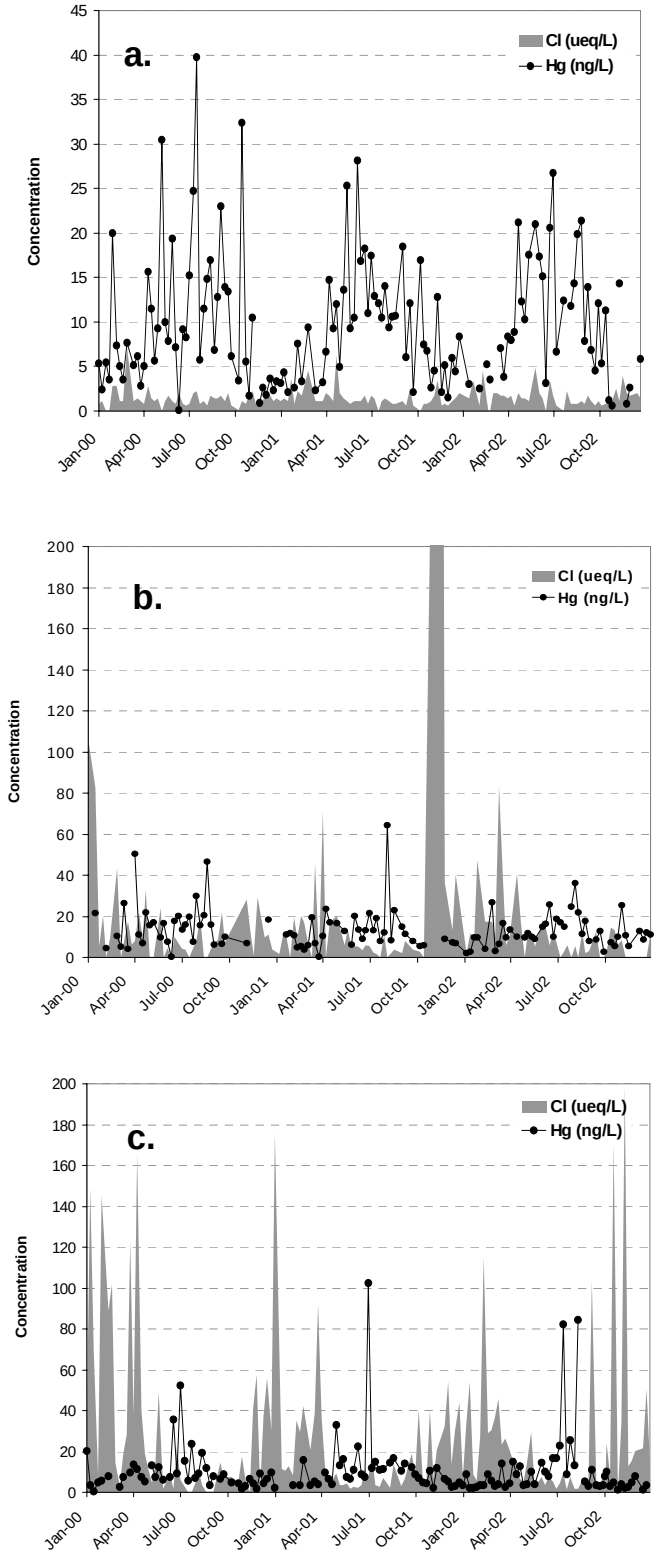


Figure 18. Hg and Cl- concentration for WI36 (a.), SC19 and SC06 (b.), and ME98 (c.) for weekly NADP and MDN wet-only precipitation collections from January 4, 2000 – December 31, 2002. Note different scale for WI36, due to low concentration of Cl-. Not shown: Cl- for 11/21/01 for SC06, ~600 μeq/L.

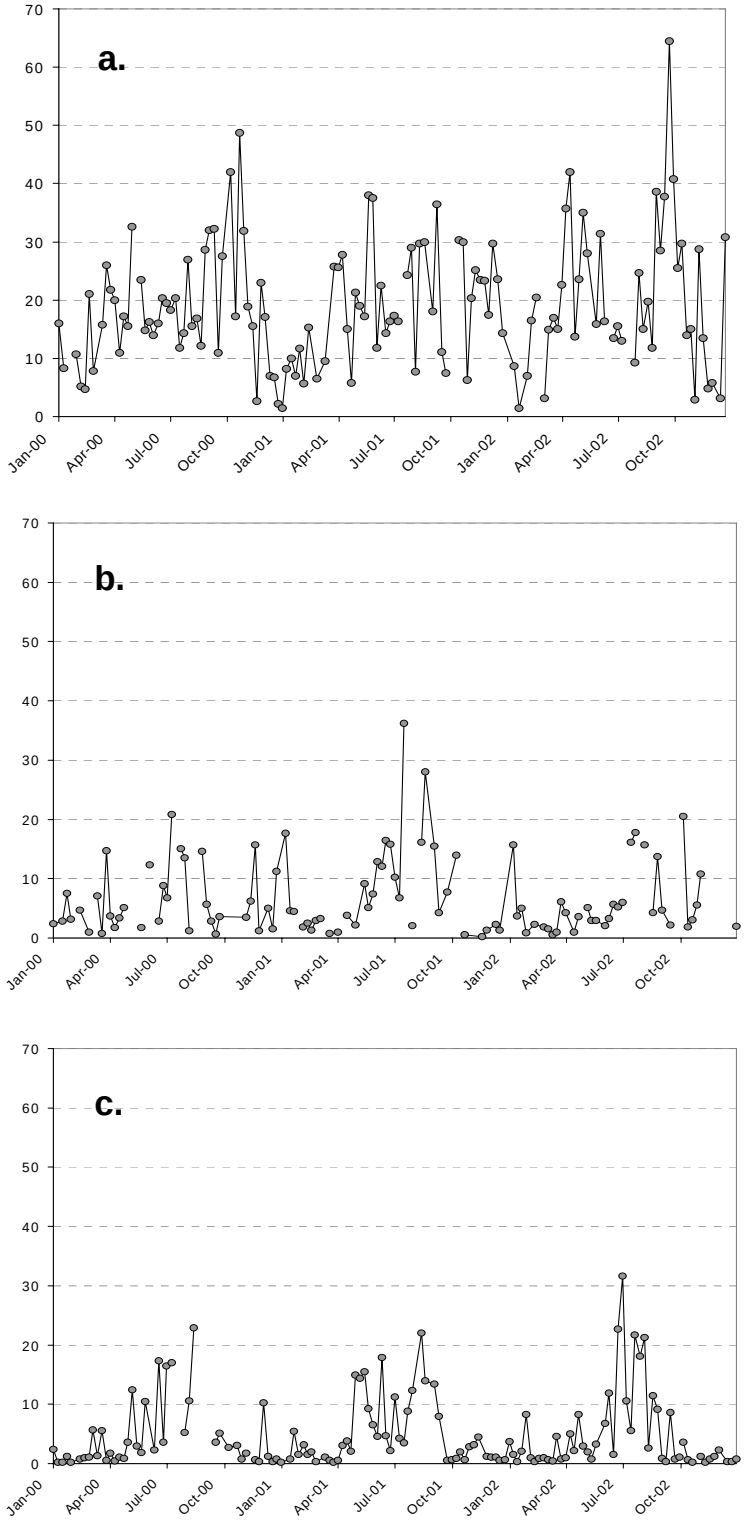


Figure 19. The ratio of SO_4^{2-}:Cl^- in weekly wet-only precipitation collections for three NADP sites: WI36 (a.), SC06 (b.), ME98 (c.) for January 4, 2000 – December 31, 2002. Site SC06 had the most discontinuous record, due to low precipitation amounts in summer.

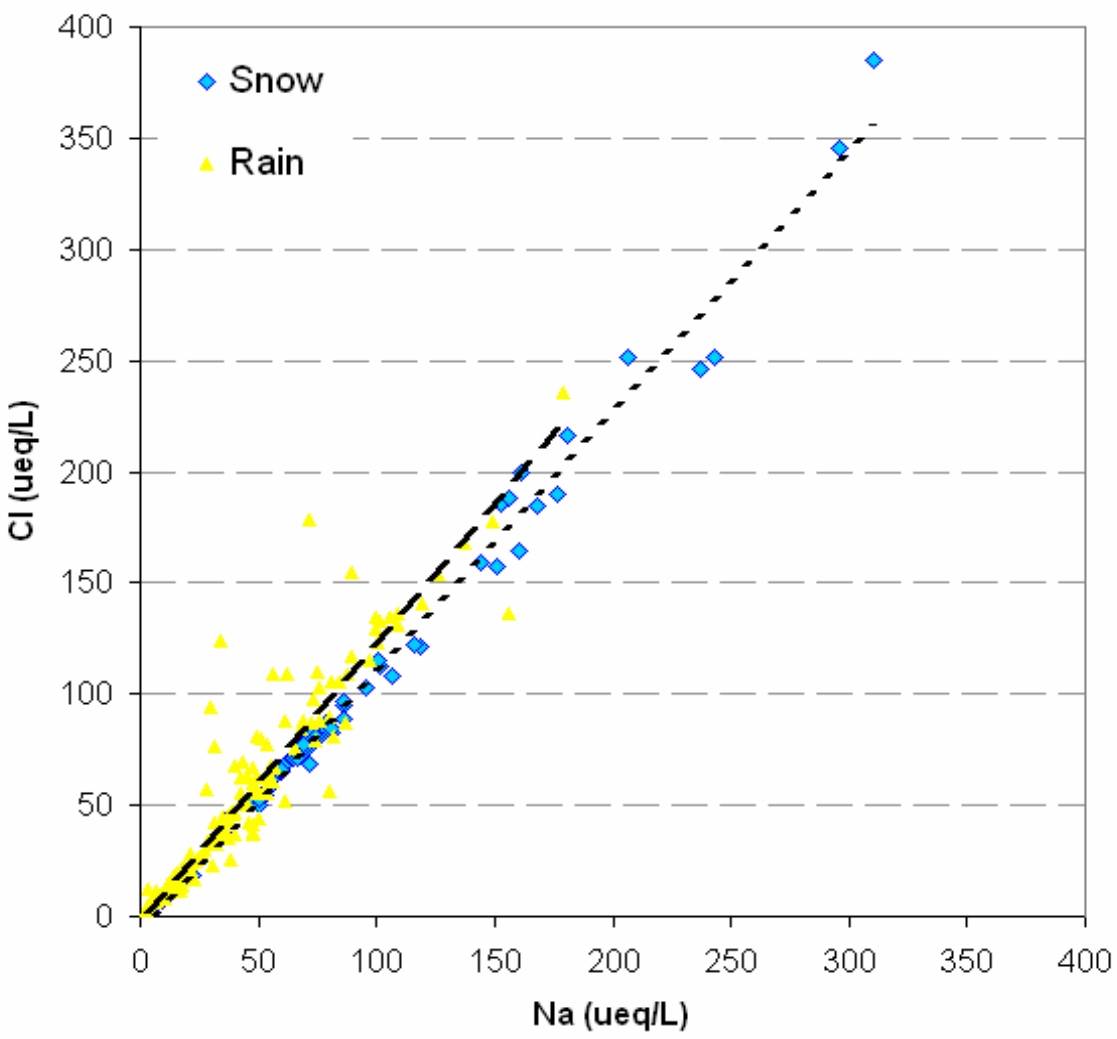


Figure 20. Sodium (Na) versus chloride (Cl) in snow and rain throughfall collected in paired watersheds at Acadia National Park, 2004-2005. Rain throughfall Na:Cl is more variable, suggesting different sources for deposition for specific events. Snow throughfall is much less variable, suggesting a more consistent source.

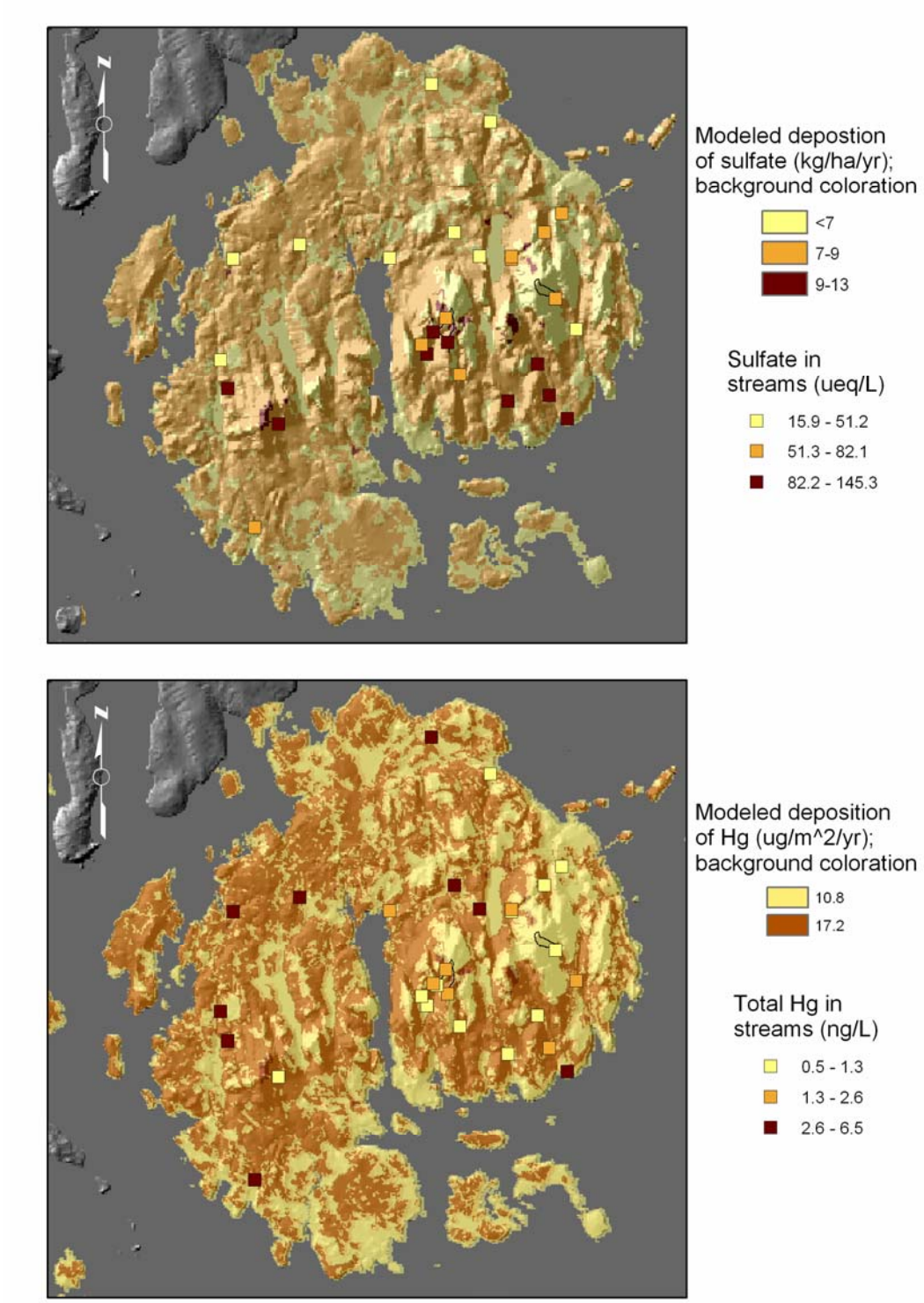


Figure 21. Modeled deposition of SO_4 (top) and Hg (bottom), determined using regression tree analysis. Only one split defined the Hg model, so only two categories of deposition are shown. Each value for deposition represents a range centered around the reported value. Streamwater concentrations for SO_4 and Hg are shown as squares, in colors matching the deposition model. Agreement between modeled deposition and streamwater concentration occurs where the color of squares matches the color of the background; for example, light yellow areas and stream values on the far eastern side of the island for Hg.

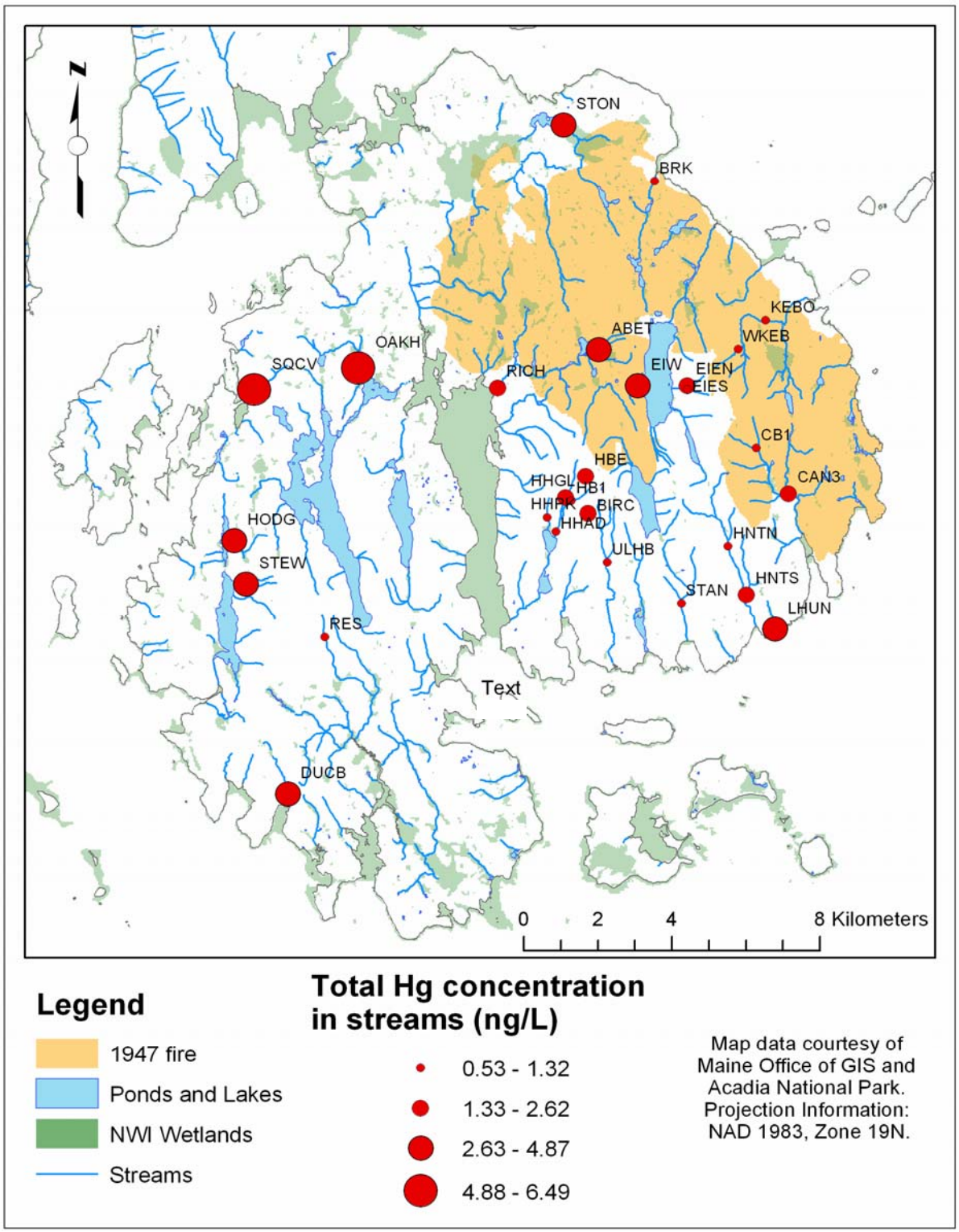
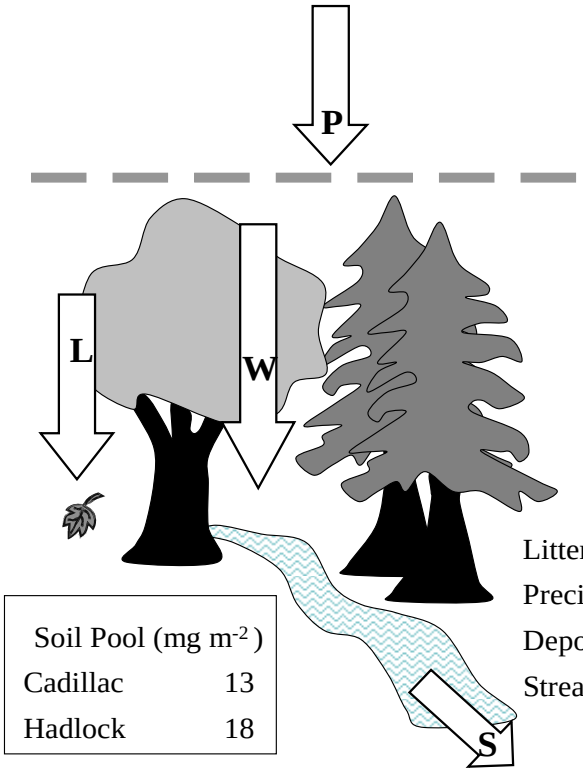


Figure 22. Total Hg concentration in 28 streams sampled October 6, 2004. Some of the lowest Hg concentrations are located within the area burned by the 1947 fire. The highest Hg concentrations are located in the northeast quadrant of the island.



Soil Pool (mg m^{-2})	
Cadillac	13
Hadlock	18

	Annual Fluxes (ug m^{-2})	
	Cadillac Brook	Hadlock Brook
Litter (L)	10.0	10.1
Precipitation (P)	6.8	6.8
Deposition (W)*	9.4	10.2
Streams (S)	0.4	1.3

Figure 23. Estimates of annual Hg flux and soil pools in the study watersheds. Precipitation flux (P) for the period of the litterfall study was measured at the ANP Mercury Deposition Network site ME98 (National Atmospheric Deposition Program, 2005). The Hg soil pool and Hg stream flux (S) were measured at these sites July 1999-2000 (Johnson, 2002; Amirbahman et al., 2004). Deposition (W)* is defined here as an estimate of annual wet deposition that included the summation of throughfall measurements from May 2000-November 2000 plus wet-only precipitation for the period November 1999-April 2000 as reported by Johnson (2002). (Figure: Sheehan, 2005)

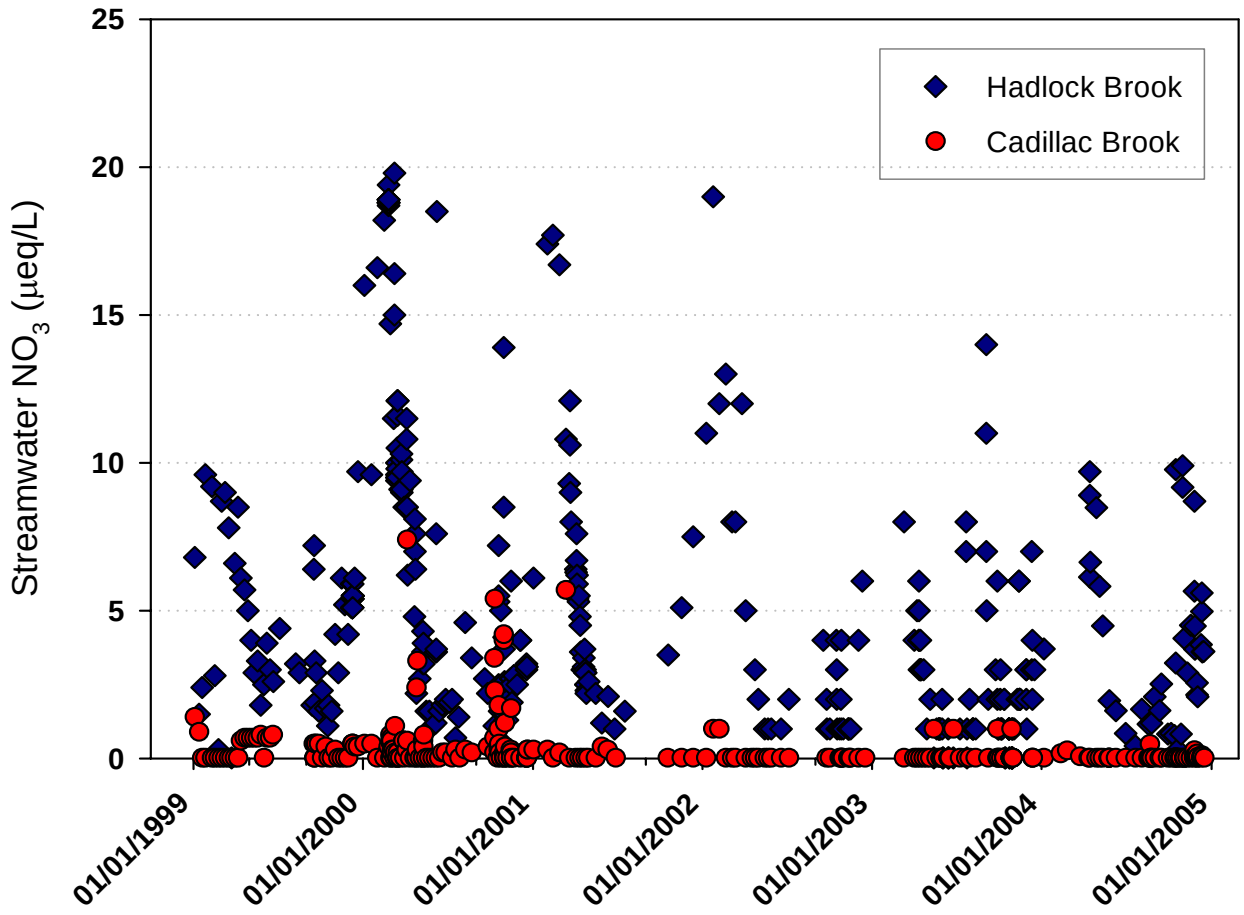


Figure 24. Nitrate (NO_3) concentration in Hadlock and Cadillac Brooks from 1998 through 2004.

7. Additional Funding Leveraged Because of Existing Long-term Data:

National Park Service Vital Signs initiative, 2005 ($12,000)
Funding awarded to continue USGS gauging at paired watershed streams

USGS Mercury Research Lab, 2004-05
In-kind award for analysis of 25 samples for isotopic and total mercury analyses to support the project: Does mercury migrate from soils to snowpack? (S.J. Nelson, D. P. Krabbenhoft, K.B. Johnson, J.S. Kahl)

National Science Foundation, 2004-2007 ($857,207)
Abiotic controls on the trophic status of oligotrophic water (S.A. Norton, I.J. Fernandez, A. Amirbahman)

National Park Service, 2003 ($20,000)
Servicewide Park Research Collaborative (SPaRC) for gauged watersheds (J.S. Kahl, P. Vaux, S. Nelson)

Association of Graduate Students Research Grant, 2003
Funds awarded to graduate student Katherine Sheehan for project work

Association of Graduate Students Research Grant, 2003
Funds awarded to S. Nelson to support laboratory analyses of bromide as a tracer for marine mercury

Canon National Parks Science Scholarship, 2003 ($78,000)
Closing the loop on hydrologic and mass balances for a temperate forested park

Margaret E. Burnham Charitable Trust, Fall 2003

Funds awarded to purchase GIS software and present water research maps on the Web

Graduate Work-Study Assistantship, 2003 ($9,010)
Funds awarded to graduate student Katherine Sheehan for project work.

Graduate Work-Study Assistantship, 2004 ($9,010)
Funds awarded to graduate student Katherine Sheehan for project work.

8. Publications and Presentations

Articles in the Popular Press and Outreach:

06/03 Bangor Daily News: *UM student tracks mercury at Acadia*. Article on Kit Sheehan's research and paired watersheds at Acadia.

10/03 National Park Service News Release: *2003 Canon National Parks Science Scholars Announced Scholarships Announced at the Vth World Parks Congress in South Africa.* Mitchell Center Ph.D. student Sarah Nelson is one of the recipients.

12/03 Bangor Daily News: *UM Grad student tracking Acadia winter trends*. Article on Canon award winner and Mitchell Center Ph.D. student Sarah Nelson.

3/04 WLBZ News: Current Water Conditions.

03-04/04 UMaine Today: *Chemicals in the Landscape*. Article on paired watersheds in Acadia and Canon scholarship.

6/04 WLBZ News coverage of sampling for mercury at Acadia National Park: Sarah Nelson, Tanya Hyssong, Paul Dumond, Catherine Schmitt.

Graduate Theses

Nelson, S.J., 2006 (expected). PhD Dissertation, University of Maine, Orono, ME.

Sheehan, K.D., 2005. Vegetative and landscape influences on forest litter Hg at Acadia NP. MS thesis, University of Maine, Orono, ME, USA. 77p.

Presentations and Abstracts Based on Data from this Cooperative Agreement:

Kahl, J.S., S. Nelson, K. Johnson, 2005. Perception experiment: paired watershed research at Acadia National Park. Gordon Research Conference field trip, July 20, 2005.

Sheehan, Katherine D., Ivan Fernandez, Aria Amirbahman and Stephen J. Kahl, 2005. Forest Litter Mercury Inputs at Acadia National Park, Maine. (Paper 4843) To be presented at the ASA-CSSA-SSSA Annual Meetings. Salt Lake City, Utah. November 6-10, 2005. In Annual meetings abstracts [CD-ROM]. ASA, CSSA, SSSA, Madison, WI.

Sheehan, K.D., April 22, 2005. Oral: Landscape and vegetative influences on mercury in forest litter at Acadia National Park. University of Maine M.S. Thesis defense, Orono, ME

Sheehan, K.D., I.J. Fernandez, A. Amirbahman, and J.S. Kahl, April 12, 2005. Oral: Litterfall mercury and the role of vegetation in forested watersheds in Acadia National Park, Maine. University of Maine Graduate Student Research Exposition, Orono, ME

Nelson, S.J., K.C. Weathers, K.B. Johnson, J.S. Kahl, 2004. Poster and abstract: Seasonal patterns and total deposition of mercury at Acadia National Park, Maine: relationships to MDN monitoring data. National Atmospheric Deposition Program 2004 Scientific

Symposium and Annual Technical Committee Meeting, Halifax, Nova Scotia, September 21-24, 2004.

Kahl, J.S., S. Nelson, and A. Grygo, 2004. Surface water chemistry data for the northeastern US for interpreting climate and acid rain trends. Northeast Ecosystems Research Consortium meeting, Durham, NH, October, 2004.

Kahl, J.S., S. Nelson, K. Johnson, K. Sheehan, T. Haines, I. Fernandez, and A. Amirbahman, 2004. Mercury biogeochemistry in gauged-paired watersheds at Acadia National Park. Invited talk, USGS 2004 Mercury Workshop, Reston VA.

Sheehan, K., May 10, 2004. Oral: Landscape and Vegetative Influences on Mercury in Forest Litter at Acadia National Park. University of Maine Thesis proposal seminar, Orono, Maine, USA.

Grygo, A., J.S. Kahl, K.E. Webster, C. Loftin, K. Tonnessen, S.J. Nelson, 2004. Poster and Abstract: Development of the SPARC Database for National Park Watershed Research: Searchable Park Access to Research Catchments. Maine Water Conference, 2004.

Kahl, J.S., and K. Tonnessen, 2003. Developing a cooperative national research network of calibrated watersheds in the National Parks. George Wright Society biannual meeting. San Diego, CA, April 14, 2003.

Nelson, S.J., J.S. Kahl, I.J. Fernandez, K.E. Webster, Cynthia S. Loftin, K.C. Weathers, 2003. Oral: Closing the loop on hydrologic and mass balances for a temperate forested park. Canon National Parks Science Scholars retreat, December 3-7 2003, Vieques, PR.

Nelson, S.J., J.S. Kahl, J.L. Campbell, C. Goodale, J. Stoddard, L.E. Rustad, S.W. Bailey, J. Kellogg, 2003. Poster: Can forest fires affect nitrogen retention for centuries? Patterns of nitrogen flux in a chronosequence of burned watersheds. Gordon Research Conference – Catchment Science, July 20-25, 2003, New London, NH.

Nelson, S.J., K.E. Webster, J.S. Kahl, K.B. Johnson, 2003. Poster: The Effects of Increasingly Variable Climate and Disturbance History on Episodic Acidification at a Coastal Maine Site, USA. American Geophysical Union Chapman Conference on Ecosystem Interaction with Land Use Change, June 14-18, 2003, Santa Fe, NM.

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Peer-reviewed Articles

Campbell, J. L., J.W. Hornbeck, M.J. Mitchell, M.B. Adams, M.S. Castro, C.T. Driscoll, J.S. Kahl, J.N. Kochenderfer, G.E. Likens, J.A. Lynch, P.S. Murdoch, S.J. Nelson, and J.B. Shanley, 2004. A Synthesis of Nitrogen Budgets from Forested Watersheds in the Northeastern United States. Water, Air, and Soil Pollution 151: 373-396.

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Documents in Review:
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As the nation's primary conservation agency, the Department of the Interior has responsibility for most of our nationally owned public land and natural resources. This includes fostering sound use of our land and water resources; protecting our fish, wildlife, and biological diversity; preserving the environmental and cultural values of our national parks and historical places; and providing for the enjoyment of life through outdoor recreation. The department assesses our energy and mineral resources and works to ensure that their development is in the best interests of all our people by encouraging stewardship and citizen participation in their care. The department also has a major responsibility for American Indian reservation communities and for people who live in island territories under U.S. administration.

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